THE SYNTHESES AND PROPERTIES OF FLUOROSUBSTITUTED TRIMETHYLAMINE-BORANES

By

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to Herb

as part of
all that is
to come

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THE SYNTHESES AND PROPERTIES OF FLUOROSUBSTITUTED TRIMETHYLAMINE-BORANES

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The fluorination of the borane portion of the Lewis acid-base adduct, trimethylamine-borane, was investigated. Highly successful and convenient methods were developed for the synthesis of the Lewis acid-base adducts, $(CH_3)_3NBH_{3-n}X_n$, where X = F and n = 1 or 2, $(CH_3)_3NBHYX$, where X = F and Y = Cl or Br (the adduct where Y = I was observed but not isolated), and $(CH_3)_3NBBrClF$.

The reaction of trimethylamine-borane and anhydrous hydrogen fluoride, which was previously known to yield only trimethylamine-trifluoroborane, was found to first yield trimethylamine-fluoroborane and trimethylamine-difluoroborane in a stepwise fluorination process. Trimethylamine-fluoroborane and trimethylamine-difluoroborane were isloated and used as precursors to the synthesis of fluorohaloborane adducts of trimethylamine. The fluorosubstituted derivatives of trimethylamine-borane completed the series of halosubstituted derivatives of trimethylamine-borane.

The chemical and physical properties of trimethylamine-fluoroborane and trimethylamine-difluoroborane along with the properties of the mixed halo derivatives of trimethylamine-borane were investigated and were discussed as a group in relationship to the properties already established by the other halo derivatives of trimethylamine-borane.

The family of fluorosubstituted trimethylamine-boranes was characterized by infrared, ^{1}H, ^{11}B, and ^{19}F nmr spectra. The ^{1}H, ^{11}B, and ^{19}F nmr spectra and the trends in spectral properties which they developed are discussed. The various spectra were used to make implications concerning the bonding within the adduct, particularly the borane postion, and the relative strength of the fluorosubstituted boranes as Lewis acids toward trimethylamine.

In the syntheses of fluorosubstituted trimethylamine-boranes, several unexpected exchange re-distribution reactions were discovered and subsequently investigated.

CHAPTER 1

INTRODUCTION

Halogen substitution for the halogens, chlorine, bromine, and iodine, on the borane portion of the Lewis acid-base adduct, trimethylamine-borane, has been well studied. The mono-, di-, and trihalogenated derivatives of trimethylamine-borane, $(CH_3)_3NBH_3$, where halogen is chlorine, bromine, or iodine, have been prepared and isolated using various halogenating agents.[1-3] Mixed dihalogenated derivatives of $(CH_3)_3NBH_3$ involving two of the halogens, chlorine, bromine, or iodine, have also been propared.[4] The mised trihalo species, trimethylamine-bromochloroiodoborane, $(CH_3)_3NBBrClI$, has been reported, but not isolated.[4]

Reports of fluorosubstituted trimethylamine-boranes, however, have been few. At the initiation of this work, the monofluoroborane and difluoroborane adducts of trimethylamine which would serve as presursors to the mixed fluorohalo trimethylamine-boranes had not been synthesized. The mixed dihalo derivatives in which one of the halogens was fluorine had been prepared in mixtures and used as mixtures in a ^1H nmr study.[5] These mixtures were the result of an exchange process involving trimethylamine-trihaloboranes and the free Lewis acid, boron trifluoride, BF_3. A mass spectral

study had been reported for the bromofluoroborane adducts of trimethylamine[6]. A mixed trihaloborane adduct of trimethylamine, where one of the halogens was flourine was not known.

Trimethylamine-trifluoroborane, $(CH_3)_3NBF_3$, was known as the only fluorosubstituted derivative of $(CH_3)_3NBH_3$. It was reported by Noeth and Beyer[1] in 1960 as the result of the reaction of trimethylamine-borane, $(CH_3)_3NBH_3$, and anhydrous hydrogen fluoride, HF. Their classic paper on the halogenation of $(CH_3)_3NBH_3$ cited $(CH_3)_3NBF_3$ to be the only product of this reaction. The reaction of $(CH_3)_3NBH_3$ and anhydrous HF was anomalous behavior for a hydrogen halide functioning as a halogenating agent towards $(CH_3)_3NBH_3$. The other hydrogen halides were known to readily achieve only monohalogenation of $(CH_3)_3NBH_3$ at room temperature.[1-3]

A primary purpose of this work was to investigate the fluorination of some amine-boranes. The effort of this work was to complete the halogenated series for $(CH_3)_3NBH_3$ with the fluoro-substituted derivatives of $(CH_3)_3NBH_3$. The halogenated series had thus far been established as the mono-, di-, and trihalo derivatives, $(CH_3)_3NBH_{3-n}X_n$, where X = Cl, Br, or I, and the mixed haloborane adducts of trimethylamine such as $(CH_3)_3NHY_{2-n}X_n$ or $(CH_3)_3NY_{3-n}X_n$, where Y or X = Cl, Br, or I.

It was necessary to first establish the existence of trimethylamine-fluoroborane, $(CH_3)_3NBH_2F$ and trimethylamine-difluoroborane, $(CH_3)_3NBHF_2$. It was hoped that once $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ were established, they could serve as precursors

to the mixed halo adducts and thereby serve to complete the full scheme of halogenation of trimethylamine-borane.

The monofluoro- and difluorosubstituted trimethylamine-boranes would be of interest not only for their role as precursors to the mixed halo derivatives of trimethylamine-borane. The chemical and physical properties of $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ along with the properties of the possible mixed halo derivatives of $(CH_3)_3NBH_3$ would be of interest as a group in relationship to the properties already established by the other halo derivatives of $(CH_3)_3NBH_3$. Since the adducts contain both boron and fluorine, the ^{19}F and ^{11}B nmr spectra would be of special interest with regard to information relating to the properties of the adduct. As a group, the fluorosubstituted borane adducts of trimethylamine might be expected to be somewhat unusual in properties since fluorine containing compounds often distinguish themselves by anomalous behavior.

During the course of synthesizing fluorosubstituted trimethylamine-borane, several unexpected exchange and re-distribution reactions were discovered. These reactions were subsequently investigated as possible synthetic routes and for information concerning the reactivity of the boron-halogen bond.

CHAPTER 2

MATERIALS AND PROCEDURES

Materials

Trimethylamine-borane was used as obtained from Callery Chemical Company. Triethylamine-borane and trimethylamine-iodoborane were prepared according to the methods of Nainan and Ryschkewitsch.[7,8] 4-picoline-borane was propared in this laboratory and kindly supplied by Bruce McMaster.

Bis-triphenylphosphineiminium chloride was prepared by Dr. C. Thorpe according to the method of Ruff and Schlientz[9] for use in this laboratory.

Anhydrous hydrogen halides were obtained from Matheson Gas Products and used as described in the experimental section.

All solvents were reagent grade and used only after drying for several days with Molecular Sieve 3A or calcium hydride.

Other chemicals used in this work were also reagent grade and unless noted were used without further purification.

Procedures

All reactions involving anhydrous hydrogen fluoride, HF, were carried out in polyethylene apparatus. The apparatus consisted of three 8 oz polyethylene bottles closely connected by polyethylene

tubing (i.d., 3/16 inch) such that the three bottles could be securely positioned in a 150 mm x 75 mm pyrex dish supported by the magnetic stirrer. The first bottle contained a convenient depth of mineral oil (approximately 2 inches) and served as a meter to control the flow rate of HF. The second bottle which will be referred to as the reaction bottle contained the solvent and the amine-borane to be halogenated. It had an additional fitting consisting of a short piece of polyethylene tubing capped with a rubber septum so that samples of the reaction solution could be easily removed by syringe for analysis by nmr. The last bottle, partially filled with a saturated solution of calcium hydroxide, served to absorb the HF which passed through the reaction bottle unreacted. This system was set-up in a well-ventilated hood and proved to be safe, efficient and convenient for the use of anhydrous HF as a fluorinating agent.

Since even slight contact of HF with flesh will cause a painful burn, extra precautions such as the wearing of double polyethylene gloves were taken to protect the worker. In case of accidental contact with HF, a mineral oil paste of magnesium oxide was kept at hand for immediate use on a flesh burn after it had been flushed with water.

All fluorine containing boranes synthesized in this work were purified by sublimation. The solid containing the borane was placed in a sublimator of appropriate size. The borane sublimed in vacuo onto a -78^{0} (dry ice/acetone) cold finger. The sublimator

was either at room temperature or it was placed in an oil bath at a higher constant temperature.

Melting points were obtained using a Thomas Hoover apparatus and reported uncorrected.

A Vacuum Atmospheres dry box (model: Dri-Train) was used for reaction requiring inert conditions.

Infrared spectra were obtained using a Beckman IR-10 spectrophotometer. Samples of the compounds were prepared for infrared analysis as KBr pellets.

^{1}H nmr spectra were obtained at 60 Hz using a Varian A60-A spectrometer. Dry methylene chloride, CH_2Cl_2, was used as the solvent unless otherwise noted. The chemical shifts are reported in Hz from tetramethylsilane which was used an the internal reference.

^{19}F nmr spectra were obtained at 94.1 MHz using a Varian XL-100 spectrometer. The chemical shifts are reported in ppm from perfluorobenzene, C_6F_6, used as an external reference.

^{11}B nmr spectra were obtained at 25.2 MHz or 32.1 MHz using a Varian XL-100 spectrometer. The chemical shifts are reported in ppm from trimethylborate, $B(OCH_3)_3$, used as an internal reference. Solutions of high concentration for both ^{11}B and ^{19}F spectra were prepared using dry methylene chloride, CH_2Cl_2, as the solvent.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

CHAPTER 3

SYNTHESES AND REACTIONS

Trimethylamine-fluoroboranes

Synthesis of trimethylamine-fluoroborane using anhydrous hydrogen fluoride.-- Trimethylamine-borane, $(CH_3)_3NBH_3$ (3.6518 g, 50.06 mmol), was placed in an 8 oz polyethylene bottle containing a magnetic stirring bar. Approximately 175 ml of dry CH_2Cl_2 were added and the reaction bottle was positioned in the apparatus previously described for the passage of HF. After the solution had stirred for a few minutes with dry nitrogen passing through the system, a 0.5 ml sample was removed by syringe for analysis by ^1H nmr. The resulting spectrum showed a single peak at 157 Hz due to the methyl resonance of $(CH_3)_3NBH_3$. The nitrogen was replaced with HF and the flow rate adjusted to a fairly fast, constant rate of approximately 30-35 bubbles in 15 seconds. An immediate and vigorous evolution of gas was observed in the reaction bottle. After a few minutes, a 0.5 ml sample was removed by syringe from the reaction bottle into an nmr tube and the spectrum was quickly taken. The spectrum showed a decrease in the peak due to the starting material and the appearance of a single new peak at 152 Hz due to the formation of trimethylamine-fluoroborane, $(CH_3)_3NBH_2F$. The

reaction was shown to accur according to the following equation.

$$(CH_3)_3NBH_3 + HF \longrightarrow (CH_3)_3NBH_2F + H_2 \qquad (3\text{-}1)$$

Since the progress of this reaction could be monitored by the ^1H nmr spectra, that is, by the disappearance of the peak due to the methyl resonance of $(CH_3)_3NBH_3$ and the appearance of the peak due to the methyl resonance of $(CH_3)_3NBH_2F$, 0.5 ml samples were removed by syringe as needed until the resulting nmr spectrum showed a single peak at 152 Hz. At this point, further addition of HF would have caused the formation of trimethylamine-difluoroborane, $(CH_3)_3NBHF_2$. Since the fluorination process is fast, the nmr spectrum must be quickly taken and closely observed in order to achieve a monofluorinated borane. Experience with the reaction enables one to judge when the HF should be replaced by nitrogen, thereby quenching the reaction.

The HF flow was replaced by a nitrogen flow when the nmr spectrum showed only a small peak at 157 Hz due to unreacted $(CH_3)_3NBH_3$. The HF present in the reaction bottle at the time of the change to nitrogen was usually sufficient to monofluorinate only the unreacted $(CH_3)_3NBH_3$. If the amount of unreacted $(CH_3)_3NBH_3$ did not equal a 1:1 molar ratio with the HF in the reaction bottle, either a small amount of $(CH_3)_3NBH_3$ or $(CH_3)_3NBHF_2$ would contaminate the desired borane, $(CH_3)_3NBH_2F$.

Monofluorination of the 50 mmol of $(CH_3)_3NBH_3$ was achieved in approximately 30 minutes. As the reaction proceeded, the solution became cloudy and a small amount of fine white solid precipitated.

The reaction bottle was then removed from the apparatus and fitted with a 2-hole rubber stopper that contained a gas inlet tube of polyethylene. Dry nitrogen was passed rapidly through the solution until white fumes ceased to be evolved.

The nmr spectrum of this solution showed a peak at 152 Hz due to $(CH_3)_3NBH_2F$ and a very small peak at 157 Hz due to the starting material, $(CH_3)_3NBH_3$, which was removed from the desired product in the purification process. Trimethylamine-borane can be more easily removed through the process of fractional sublimation than $(CH_3)_3NBHF_2$. The other feature of the spectrum was a doublet positioned at 174 and 179 Hz which is characteristic of an ammonium salt.

Dry nitrogen was passed until the solvent was removed and the white solid which remained was first observed to be dry. Prolonged exposure to a stream of nitrogen at this point would have resulted in loss of the desired product as the fluorinated boranes have a relatively high volatility at room temperature. The white solid was transferred to a large sublimator. Trimethylamine-fluoroborane was allowed to sublime in vacuo at room temperature onto a dry ice/acetone cold finger. The yield of $(CH_3)_3NBH_2F$ was 3.846 g, 42.31 mmol, which was 85% of the amount calculated based on $(CH_3)_3NBH_3$.

Trimethylamine-fluoroborane is a white crystalline solid, mp 113°. Anal. Calcd. for $(CH_3)_3NBH_2F$: C, 39.62; H, 12.19; N, 15.40; F, 20.89. Found: C, 39.39; H, 12.24; N, 15.19; F, 20.97.

The infrared spectrum of $(CH_3)_3NBH_2F$ is described in Table 3-1 and shown in Figure 3-1. The most characteristic feature of the

spectrum is the doublet centered at 2300 cm^{-1}. This doublet is the result of the symmetric and asymmetric B-H stretching for the $-BH_2$ portion of the molecule.

The ^{11}B nmr spectrum which is shown in Figure 3-2 consisted of a sextet of intensity 1:1:2:2:1:1 centered at 12.9 ppm upfield from $B(OCH_3)_3$ with J_{BH}=115 Hz and J_{BF} = 90 Hz as the observed coupling constants.

The ^{19}F nmr spectrum which is shown in Figure 3-3 consisted of a nonet of intensity 1:2:2:2:2:2:2:2:1 centered at 40.8 ppm upfield from C_6F_6 with J_{BF}=90 Hz and J_{HBF}=45 Hz as the observed coupling constants.

The above physical data for $(CH_3)_3NBH_2F$ have been confirmed by the work of J. M. VanPaasschen and R. A. Geanangel published 6 months after this work was completed.[10]

The passage of HF through the CH_2Cl_2 solution also produced a white solid which though somewhat soluble in CH_2Cl_2 was non-sublimable and hence easily separated from the desired borane. This white solid was found to be trimethylammonium tetrafluoroborate. Anal. Calcd. for $(CH_3)_3NH^+BF_4^-$: C, 24.53; H, 6.86; N, 9.53; F, 51.72. Found: C, 24.41; H, 6.82; N, 9.53; F, 51.48.

The infrared spectrum of $(CH_3)_3NH^+BF_4^-$ which is shown in Figure 3-4 indicates a strong band at 2700 cm^{-1} due to N-H stretching. The sharp doublet at 520 and 530 cm^{-1} and broad band at 1000 cm^{-1} are the characteristic absorptions of BF_4^- [11].

Synthesis of trimethylamine-fluoroborane using a methylene

chloride solution of hydrogen fluoride.-- Trimethylamine-borane, $(CH_3)_3NBH_3$ (0.8345 g, 11.44 mmol), was placed in an 8 oz polyethylene bottle containing approximately 50 ml of dry CH_2Cl_2 and a magnetic stirring bar. The polyethylene bottle was placed on a magnetic stirrer and the solution was allowed to stir for several minutes before 0.5 ml of solution was removed as an nmr sample. The nmr spectrum showed a single peak at 157 Hz due to the starting material $(CH_3)_3NBH_3$. Twenty-five ml of a CH_2Cl_2 solution of HF (0.57M) was quickly added to the bottle. The HF solution was freshly prepared by passing HF through dry CH_2Cl_2 and titrated just prior to use with 1.0 M NaOH. Gas evolution began immediately on addition of the solution of HF and continued at a moderate rate for approximately 20 minutes, during which time the solution was kept stirring and the reaction bottle lightly capped. The nmr spectrum of the reaction at this point indicated only a small peak at 157 Hz due to unreacted starting material. The other peak was at 152 Hz and due to $(CH_3)_3NBH_2F$. The volume of HF solution originally added provided 0.29 mmol of HF in excess of the amount required for a 1:1 stoichiometry of the reactants. Using the nmr spectra as a measure of the extent of reaction, further additions (one of 5 ml and two of 1 ml) were made providing another 0.40 mmol of HF. Finally, a nmr spectrum of a sample of the reaction solution showed the best possible symmetrical peak attributable to $(CH_3)_3NBH_2F$. The solvent was removed by nitrogen and the remaining white solid transferred to a large sublimator. Trimethylamine-fluoroborane (0.821 g,

9.106 mmol), was sublimed in vacuo onto the dry ice/acetone cold finger in a yield of 82% based on the amount of $(CH_3)_3NBH_3$.

This method of preparation of $(CH_3)_3NBH_2F$ is not as convenient as the reaction using anhydrous HF since the HF solution must be freshly made and titrated as it quickly changes concentration on standing. Also, for reasonable yields, a molarity near to 0.50 must be used.

Synthesis of trimethylamine-difluoroborane.-- Trimethylamine-borane, $(CH_3)_3NBH_3$ (3.9352 g, 41.61 mmol), was placed in an 8 oz polyethylene bottle containing a magnetic stirring bar. Approximately 175 ml of dry CH_2Cl_2 were added and the reaction bottle was positioned in the apparatus for the passage of HF. After the solution had stirred for a few minutes with dry nitrogen passing through the system, a 0.5 ml sample was removed by syringe for analysis by ^1H nmr. The resulting spectrum showed a single peak at 157 Hz due to the methyl resonance of $(CH_3)_3NBH_3$. The nitrogen was replaced with HF and flow adjusted to a fairly rapid rate of approximately 35 bubbles in 15 seconds.

After a few minutes of vigorous gas evolution, a 0.5 ml sample was syringed from the reaction bottle into an nmr tube. The nmr spectrum showed a decrease in the peak due to the starting material and the appearance of a new peak at 152 Hz due to the formation of $(CH_3)_3NBH_2F$ according to equation 3-1. Subsequent 0.5 ml aliquots sampled at approximately 5-minute intervals showed a steady decrease of the starting material peak at 157 Hz and a steady growth of the

peak due to $(CH_3)_3NBH_2F$ at 152 Hz until a spectrum showed almost no remaining $(CH_3)_3NBH_3$, but only $(CH_3)_3NBH_2F$. Gas evolution continued in the reaction bottle and the nmr spectrum of the next sample showed a decrease in intensity of the peak at 152 Hz due to $(CH_3)_3NBH_2F$ and the appearance of a new peak at 148 Hz due to the formation of trimethylamine-difluoroborane, $(CH_3)_3NBHF_2$. The reaction which produced $(CH_3)_3NBHF_2$ proved to proceed by the following equation.

$$(CH_3)_3NBH_2F + HF \longrightarrow (CH_3)_3NBHF_2 + H_2 \qquad (3\text{-}2)$$

The fluorination process was continued until the nmr spectrum of a sample of the reaction solution showed only a peak at 148 Hz, but slightly skewed towards 152 Hz. The HF flow was then replaced by nitrogen and the difluorination was completed by the HF present in the reaction bottle when the HF flow was replaced by nitrogen. The progress of the reaction was closely monitored by the nmr spectra so that excess HF was avoided.

Further fluorination in the preparation of $(CH_3)_3NBHF_2$ is easier to avoid than in the preparation of $(CH_3)_3NBH_2F$ as there appears to be a slight decrease in the reactivity of the borane as it becomes successively more fluorinated.

The HF flow was stopped and the reaction bottle was removed from the apparatus and positioned such that a stream of nitrogen was allowed to evaporate the solution just to dryness leaving a fine white solid. The white solid was immediately transferred to a large sublimator and the $(CH_3)_3NBHF_2$ allowed to sublime in vacuo onto a dry ice/acetone cold finger thus separating it from the non-

sublimable other product of the reaction, $(CH_3)_3NH^+BF_4^-$. The yield of $(CH_3)_3NBHF_2$ was 3.1627 g, 29.03 mmol, which was 70% of the amount calculated based on $(CH_3)_3NBH_3$. The yield of the ammonium salt $(CH_3)_3NH^+BF_4^-$ was 1.4386, 9.786 mmol. The two products accounted for 96% of the boron in the starting material.

Trimethylamine-difluoroborane is a white crystalline solid, mp 123°. Anal. Calcd. for $(CH_3)_3NBHF_2$: C, 33.07; H, 9.25; N, 12.86; F, 34.88. Found: C, 32.97; H, 9.35; N, 12.73; F, 34.78.

The infrared spectrum of $(CH_3)_3NBHF_2$ is described in Table 3-1 and shown in Figure 3-5. The characteristic B-H stretching region of this spectrum showed the expected singlet near 2400 cm^{-1}.

The ^{11}B nmr spectrum as shown in Figure 3-6 consisted of a quintet of intensity 1:2:2:2:1 centered at 14.9 ppm upfield from $B(OCH_3)_3$ with J_{BH} = 144 Hz and J_{BF} = 71 Hz as the observed coupling constants.

The ^{19}F nmr spectrum as shown in Figure 3-7 consisted of a quintet of intensity 1:2:2:2:1 centered at 0.7 ppm downfield from C_6F_6 with J_{BF} = 71 Hz and J_{HBF} = 71 Hz as the observed coupling constants.

As for $(CH_3)_3NBH_2F$, the physical data for $(CH_3)_3NBHF_2$ were confirmed subsequent to this work by J. M. Van Paasschen and R. A. Geanangel.[10]

Reaction of trimethylamine-borane and a methylene chloride solution of hydrogen fluoride in a molar ratio of 1:2.-- Trimethylamine-borane, $(CH_3)_3NBH_3$ (0.9067 g, 12.43 mmol), was dissolved in

50 ml of dry CH_2Cl_2 in an 8 oz polyethylene bottle. On the basis of a 2:1 stoichiometry of HF to $(CH_3)_3NBH_3$, 30 ml of a freshly prepared and titrated CH_2Cl_2 solution (0.75M) were added. Only a slow rate of gas evolution was observed. The nmr spectrum of a sample of the reaction solution removed when gas evolution had ceased showed incomplete difluorination of $(CH_3)_3NBH_3$. Hence, further additions of the methylene chloride solution of HF were made. After the reaction following each addition subsided, a sample of the solution was removed for analysis by ^1H nmr. For this reaction, three additions of HF solution of 10 ml each were made to achieve a reaction solution for which the nmr spectrum indicated only $(CH_3)_3NBHF_2$ and ammonium salt. The additional solution of HF provided twice the molar amount of HF required for the difluorination of $(CH_3)_3NBH_3$. This method of preparation for $(CH_3)_3NBHF_2$ was found much less satisfactory than the difluorination of $(CH_3)_3NBH_3$ using anhydrous HF.

Reaction of trimethylamine-borane and a methylene chloride solution of hydrogen fluoride in a molar ratio of 1:3.-- Trimethylamine-borane, $(CH_3)_3NBH_3$ (0.9449 g, 12.95 mmol), was dissolved in 50 ml of dry CH_2Cl_2 in an 8 oz polyethylene bottle. Seventy-five ml of freshly prepared and titrated CH_2Cl_2 solution (0.75M) were added. The reaction bottle was lightly capped and was left overnight with the solution gently stirring. The addition of HF solution provided 19 mmol of HF in excess of the amount of HF required by a 3:1 stoichiometry for trifluorination of $(CH_3)_3NBH_3$. The nmr spectrum of the final solution showed a large peak at 148 Hz due to

$(CH_3)_3NBHF_2$ and only a slight and broadened peak at 157 Hz that could be attributed to the methyl resonance of trimethylamine-trifluoroborane, $(CH_3)_3NBF_3$.

Reaction of trimethylamine-trifluoroborane and anhydrous hydrogen fluoride.-- Trimethylamine-trifluoroborane, $(CH_3)_3NBF_3$ (0.2211 g, 1.742 mmol), was dissolved in 80 ml of CH_2Cl_2 which had been freshly filtered from calcium hydride, CaH_2. Using the polyethylene apparatus previously described, HF was passed through the system for 30 minutes. The polyethylene bottle was then capped and was left at room temperature for several days. When the bottle was opened, the solution fumed intensely on being exposed to the atmosphere. The nmr spectrum of this solution was identical to that of the starting solution. The main feature of this spectrum was the multiplet* characteristic of $(CH_3)_3NBF_3$ at 157 Hz. Even after six days, the solution fumed when the polyethylene bottle was opened. The nmr spectra of the solution remained unchanged. The solvent was removed by nitrogen and 0.1681 g of $(CH_3)_3NBF_3$, 76% of the starting amount was collected by sublimation in vacuo at room temperature. Only a small amount of the solid did not sublime. This residue deliquesced immediately but was identified by solution infrared as the ammonium salt, $(CH_3)_3NH^+BF_4^-$.

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* The multiplicity that has been observed in the ^1H nmr as identifying characteristic for the methyl resonance of $(CH_3)_3NBF_3$ has been described and accounted for on the basis of coupling of the methyl proton to both the ^{11}B and ^{19}F nuclei. Under high resolution, the methyl peak of $(CH_3)_3NBF_3$ has been observed as a 1:3:4:4:4:4:4:3:1 decet[12,13].

Reaction of triethyloxoniumtetrafluoroborate and trimethylamine-borane.-- Triethyloxoniumtetrafluoroborate, $(C_2H_5)_3O^+BF_4^-$, was prepared according to the method of Meerwin[14] under inert conditions in a yield of 84%. It was stored under ether in small glass screwcap vials in a refrigerator. For each usage a portion of the solid was transferred in a dry box to a small round bottom flask that was fitted with a vacuum line adapter. The flask was then attached to a vacuum line for removal of ether and then returned to the dry box for immediate use.

In a dry box, triethyloxoniumtetrafluoroborate, $(C_2H_5)_3O^+BF_4^-$ (0.060 g, 0.311 mmol), and trimethylamine-borane $(CH_3)_3NBH_3$ (0.023 g, 0.315 mmol), were placed in an nmr tube. On addition of 1 ml of dry CH_2Cl_2, there was immediate gas evolution. The reaction was expected to occur according to the following equation.

$$(C_2H_5)_3O^+BF_4^- + (CH_3)_3NBH_3 \rightarrow C_2H_6 + (CH_3)_3N\overset{H}{\underset{H}{B}}O(C_2H_5)_2{}^+BF_4^- \qquad (3\text{-}3)$$

The gas evolved was ethane, as expected, and was identified by its chemical shift in the ^1H nmr. However, the nmr spectrum showed new peaks at 152 Hz and 148 Hz, slightly upfield from the peak at 157 Hz for the methyl resonance of the starting material, $(CH_3)_3NBH_3$. The peak at 157 Hz decreased rapidly during the initial part of the reaction and then increased at the expense of the peaks at 148 Hz and 152 Hz as the reaction continued. The peak at 148 Hz was not observed in the spectrum during the initial few minutes of reaction but then gradually defined itself from an upfield skewing

of the peak at 152 Hz. The starting material peak at 157 Hz reached a minimum approximately 15 minutes after mixing and then began a slow steady increase at the expense of the peaks at 148 Hz and 152 Hz. The peak at 157 Hz remained symmetrical with no indication of multiplicity.

It should be noted that even though $(CH_3)_3NBH_3$ and $(CH_3)_3NBF_3$ have identical chemical shifts in the ^1H nmr, if CH_2Cl_2 is the solvent, they are easily distinguished by peak appearance. The spectrum of $(CH_3)_3NBF_3$ is a broad peak with a characteristic multiplicity whereas the spectrum of $(CH_3)_3NBH_3$ is a single symmetrical peak. If, however, a sample of $(CH_3)_3NBF_3$ contains a small amount of $(CH_3)_3NBH_3$, the peak at 157 Hz appears as a singlet.

After 100 minutes, all three peaks were present in the spectrum. The peak at 157 Hz was the most intense. A duplicate of this reaction mixture was prepared and the nmr tube was allowed to remain at room temperature with electrical tape wrapping the plastic cap. After 27 days the spectrum showed only a peak at 157 Hz. This peak had the multiplicity characteristic of $(CH_3)_3NBF_3$. Another duplicate of this reaction was done but with 0.5 ml of ether replacing 0.5 ml of the solvent, CH_2Cl_2. Similar observations were made of the nmr spectrum, only the peak evolvement was much slower.

In these reactions, the ethyl peaks of the starting material disappeared almost immediately. In the reactions without ether, a single quartet and triplet resulting from the ethyl group of the product appeared immediately at 253 Hz and 83 Hz. This ethyl

resonance was identical to the chemical shift of the ethyl group in boron trifluoride etherate, $(C_2H_5)_2O{\cdot}BF_3$. As the reaction proceeded, there was an upfield shift of a few cycles for this resonance to 247 Hz and 81 Hz. In the reaction containing ether, there was again a single set of ethyl peaks but occurring at 229 Hz and 75 Hz.

The species responsible for the new peaks, 152 Hz and 148 Hz, were found to be volatile and so alike in properties that they appeared non-separable. The products of this reaction suggested fluorinated trimethylamine-boranes rather than the salt of the ether containing cation that was originally expected.

Hartman and Miller had reported the ^1H nmr chemical shifts for trimethylamine-chlorofluoroboranes which they prepared as equilibrium mixtures from the trimethylamine adduct of boron trichloride and free Lewis acid, boron trifluoride.[5] Therefore, a reaction was done to chlorinate any trimethylamine-fluoroboranes which were produced in a 1:1 mixture of $(CH_3)_3NBH_3$ and $(C_2H_5)_3O^+BF_4^-$. As described above, the reaction of 0.311 mmol of $(C_2H_5)_3O^+BF_4^-$ and 0.315 mmol of $(CH_3)_3NBH_3$ in CH_2Cl_2 was repeated. The ^1H nmr spectrum of this reaction mixture again showed single peaks at 148 Hz, 152 Hz, and 157 Hz. Chlorine, Cl_2, was passed through this solution until a light yellow coloration persisted. The ^1H nmr spectrum of this solution showed the disappearance of the peaks at 148 Hz and 152 Hz and the appearance of three new peaks at 179 Hz, 170 Hz, and 162 Hz. Of these, the peak at 170 Hz was the most intense. The peak at 157 Hz had decreased in intensity but also had become the broad multi-

plet characteristic of $(CH_3)_3NBF_3$. The new peaks at 179 Hz, 170 Hz, and 162 Hz were all quartets, indicative of trihalo species. According to Hartman and Miller, these shifts were assigned as $(CH_3)_3NBCl_3$, $(CH_3)_3NBCl_2F$, and $(CH_3)_3NBClF_2$ respectively.[5]

Another mixture of 0.311 mmol of $(C_2H_5)_3O^+BF_4^-$ and 0.315 mmol of $(CH_3)_3NBH_3$ in CH_2Cl_2 was stirred overnight with several grams of sodium fluoride, NaF. The nmr spectrum of the solution showed again a single set of ethyl peaks attributable to free ether. The predominant new peak was at 152 Hz but it was unsymmetrical with a slight bulge on the upfield side. The other new peak at 157 Hz again appeared as a singlet. This reaction was also done with the $(CH_3)_3NBH_3$ in a two-fold and eight-fold excess over the oxonium salt. The initial nmr spectrum of both reaction mixtures showed a new peak at 152 Hz. However, after the solution remained for a time at room temperature, the nmr spectrum showed the development of a peak at 148 Hz.

In conjunction with this series of experiments, it was found that no reaction occurred between $(CH_3)_3NBH_3$ and $BF_3\cdot(C_2H_5)_2O$. The nmr spectrum of trimethylamine-iodoborane, $(CH_3)_3NBH_2I$, was also observed to remain unchanged when a CH_2Cl_2 solution of it was stirred overnight with NaF.

Reaction of bis-triphenylphosphineiminium fluoride with trimethylamine-iodoborane.-- Bis-triphenylphosphineiminium fluoride, $((C_6H_5)_3P)_2NF$, was prepared by the conversion of $((C_6H_5)_3P)_2NCl$ to $((C_6H_5)_3P)_2NF$ using an aqueous solution of silver fluoride, AgF.

The product of this conversion was then placed in a drying pistol and dried at 100° over P_2O_5 for 24 hours. In a dry box, 0.045 g, 0.0807 mmol, of the converted salt, $((C_6H_5)_3P)_2NF$, was weighed into an nmr tube and 1.0 ml of a freshly prepared stock solution of $(CH_3)_3NBH_2I$ added so that a 1:1 stoichiometry of reactants existed. Within 10 minutes of mixing, an nmr spectrum of the solution showed two new peaks. The most intense peak was at 152 Hz indicating $(CH_3)_3NBH_2F$ with a much smaller peak at 159 Hz due to trimethylamine-chloroborane, $(CH_3)_3NBH_2Cl$. There was also some unreacted starting material as indicated by the peak at 169 Hz. After 1 hour at room temperature the nmr spectrum showed a slight increase in the peaks at 152 Hz and 159 Hz at the expense of the peak at 169 Hz. After 24 hours no starting material remained. The problem for this exchange reaction as a possible route to the synthesis of $(CH_3)_3NBH_2F$ was the incomplete conversion of the chloride to the fluoride iminium salt as evidenced by the presence of $(CH_3)_3NBH_2Cl$ in the reaction mixture.

Bis-triphenylphosphineiminium fluoride was more successfully prepared by another method. Anhydrous hydrogen fluoride was condensed onto a small amount of $((C_6H_5)_3P)_2NCl$ in a polyethylene bottle surrounded by an ice bath at 0°. The amount of liquid HF necessary for conversion was approximated on the basis of the density of liquid HF(d = 1 g/ml, 1 ml = 50 mmol). When the amount of liquid HF was judged to be in excess of a 1:1 molar ratio with the salt, the ice bath was removed and the flow of HF was replaced

by nitrogen. When the mixture had evaporated to dryness, a white solid remained which was considered to be the fluoride salt.

The reaction of $((C_6H_5)_3P)_2NF$ and $(CH_3)_3NBH_2I$ in CH_2Cl_2 was repeated using the iminium fluoride as prepared above. After this reaction mixture had remained at room temperature for 3 hours, the ^1H nmr spectrum showed the expected peak at 152 Hz due to $(CH_3)_3NBH_2F$. There was also a very small peak at 159 Hz indicating a slight amount of $(CH_3)_3NBH_2Cl$ in the reaction mixture. The desired product, $(CH_3)_3NBH_2F$, was easily collected by the usual sublimation procedure.

Trimethylamine-chlorofluoroboranes

Synthesis of trimethylamine-chlorofluoroborane.-- Trimethylamine-monofluoroborane, $(CH_3)_3NBH_2F$ (1.0048 g, 11.1 mmol), was placed in a 100 ml 3-neck flask fitted with a gas inlet tube, rubber septum, and drying tube filled with Drierite and which contained a magnetic stirring bar and 50 ml of CH_2Cl_2, freshly filtered from CaH_2. The gas inlet was fitted with a Y-connection so that hydrogen chloride, HCl, and nitrogen could be easily and alternately passed through the solution. The nmr spectrum of the solution showed a single peak at 152 Hz due to the starting material, $(CH_3)_3NBH_2F$. After approximately 10 minutes, the nitrogen was replaced with HCl. Gas evolution began as soon as the HCl was in contact with the solution and its rate was dependent on the flow rate of HCl. The reaction proved to proceed according to

the following equation.

$$(CH_3)_3NBH_2F + HCl \rightarrow (CH_3)_3NBHClF + H_2 \qquad (3\text{-}4)$$

When gas evolution had ceased, the HCl was replaced by nitrogen and the solution was allowed to evaporate to dryness leaving a white solid. The nmr spectrum of this solution showed a single new peak at 156 Hz. The doublet at 168 Hz and 172 Hz, characteristic of an ammonium salt, was also present in the spectrum.

The white solid was transferred to a large sublimator for purification. The sublimator was placed in an oil bath maintained at 35-40° and the desired product, trimethylamine-chlorofluoroborane, $(CH_3)_3NBHClF$, was allowed to sublime in vacuo onto a dry ice/acetone cold finger. The yield of $(CH_3)_3NBHClF$ was 1.1022 g or 88% of the amount based on $(CH_3)_3NBH_2F$.

Trimethylamine-chlorofluoroborane, $(CH_3)_3NBHClF$, is a white crystalline solid, mp 103-104°. Anal. Calcd. for $(CH_3)_3NBHClF$: C, 28.74; H, 8.04; N, 11.17; F, 15.15; Cl, 28.28. Found: C, 28.86; H, 8.30; N, 10.92; F, 14.97; Cl, 28.46.

The infrared spectrum of $(CH_3)_3NBHClF$ is described in Table 3-1 and shown in Figure 3-8. As would be characteristically expected, the B-H stretch occurred as a singlet at 2400 cm^{-1}.

The ^{11}B nmr spectrum as shown in Figure 3-9 consisted of a quartet of intensity 1:1:1:1 centered at 12.1 ppm upfield from $B(OH_3)_3$ with J_{BH} = 155 Hz and J_{BF} = 82 Hz as the observed coupling constants.

The ^{19}F nmr spectrum as shown in Figure 3-10 consisted of an

octet of intensity 1:1:1:1:1:1:1:1 centered at 0.9 ppm downfield from C_6F_6 with J_{BF} = 82 Hz and J_{HBF} = 53 Hz as the observed coupling constants.

In another preparation, the nmr spectrum of the final reaction solution showed a small peak at 148 Hz which had been present in and masked by the peak of the starting material at 152 Hz. To rid the system of this impurity, the reaction solution, saturated with HCl, was allowed to remain at room temperature for a day or two until the peak at 148 Hz was no longer present in the nmr spectrum. Such conditions did not affect the desired product, $(CH_3)_3NBHClF$.

Reaction of trimethylamine-chlorofluoroborane and anhydrous hydrogen fluoride.-- Trimethylamine-chlorofluoroborane, $(CH_3)_3NBHClF$ (0.5561 g, 4.435 mmol), was dissolved in 175 ml of dry CH_2Cl_2 contained in an 8 oz polyethylene bottle. Using the procedure previously described, the passage of HF was begun at a moderate rate. Samples (0.5ml) were removed by syringe for analysis by ^1H nmr at 10-minute intervals to monitor the progress of the reaction. The first spectrum showed a decrease in the starting material peak at 156 Hz and the appearance of a new peak at 148 Hz due to $(CH_3)_3NBHF_2$. At the end of 30 minutes the reaction mixture was almost entirely $(CH_3)_3NBHF_2$. Continued passage of HF resulted in a broad multiplet at 157 Hz identifiably characteristic of $(CH_3)_3NBF_3$. The solvent was evaporated to dryness leaving a white solid which, when transferred to a sublimator, yielded 0.4119 g, 32.45 mmol, of sublimed, white, crystalline solid identified to be $(CH_3)_3NBF_3$. The yield was 73% based on the amount of $(CH_3)_3NBHClF$.

Reaction of trimethylamine-chloroborane with anhydrous hydrogen fluoride.-- Trimethylamine-chloroborane, $(CH_3)_3NBH_2Cl$ (1.0889 g, 10.39 mmol), was dissolved in 175 ml of dry CH_2Cl_2 contained in an 8 oz polyethylene bottle which was positioned in the apparatus for the passage of HF. The nmr spectrum of this starting solution showed a single peak at 158 Hz due to the methyl resonance of $(CH_3)_3NBH_2Cl$. After 5 minutes of HF at a moderate rate, the nmr spectrum showed no change. During the next 10- to 15-minute interval there was a small amount of gas evolution. The nmr spectrum now showed a new peak 1 or 2 cycles upfield which appeared as a bulge on the upfield side of the starting material peak. After a total of 25 minutes of HF flow, the nmr spectrum showed a continued development of the peak at 156 Hz considered to be $(CH_3)_3NBHClF$, and another new well-defined peak at 148 Hz indicative of $(CH_3)_3NBHF_2$. However, there was no peak discernible at 152 Hz for $(CH_3)_3NBH_2F$. The HF flow was continued with no other peaks, such as for $(CH_3)_3NBClF_2$ at 163 Hz, appearing. The intensity of the peak at 148 Hz due to $(CH_3)_3NBHF_2$ reaches a maximum after about 45 minutes of HF passage. Further HF reduced its intensity and changed the appearance of the spectrum at 157-158 Hz to that of the broad multiplet characteristic of $(CH_3)_3NBF_3$. The nmr spectrum of the final solution through which HF had passed for 70 minutes showed that the only peak attributable to a trimethylamine-borane was at 157 Hz and was due to $(CH_3)_3NBF_3$.

In another experiment of similar conditions, the $(CH_3)_3NBF_3$ collected by sublimation gave a yield of 70% based on the amount

of $(CH_3)_3NBH_2Cl$.

Reaction of trimethylamine-difluoroborane and gaseous hydrogen chloride.-- Trimethylamine-difluoroborane, $(CH_3)_3NBHF_2$ (0.5312 g, 48.77 mmol), was dissolved in 175 ml of dry CH_2Cl_2 contained in an 8 oz polyethylene bottle. Using the apparatus set up for the passage of HF, a moderate flow rate of HCl was begun through the solution. Nmr spectra of samples of the reaction solution showed that the peak at 148 Hz due to the starting material, $(CH_3)_3NBHF_2$, gradually decreased and finally disappeared from the spectrum. No other peak appeared in the spectrum except what could be attributed to an ammonium salt.

Synthesis of trimethylamine-chlorodifluoroborane.-- Freshly sublimed trimethylamine-difluoroborane, $(CH_3)_3NBHF_2$ (0.6248 g, 5.735 mmol), was dissolved in 50 ml of dry CH_2Cl_2 contained in a 2-neck, 100 ml flask fitted with a gas inlet tube and drying tube containing Drierite. Chlorine was bubbled through the solution until a permanent yellow coloration was achieved. The following reaction was shown to have occurred.

$$(CH_3)_3NBHF_2 + Cl_2 \rightarrow (CH_3)_3NBClF_2 + HCl \qquad (3\text{-}5)$$

The nmr spectrum of this solution showed a broad doublet at 162 Hz. On an expanded scale it was resolved to a quartet which is characteristic for the methyl absorptions of trihalogenated trimethylamine-boranes[15-16]. The chlorine was replaced with nitrogen and the solution evaporated to dryness leaving a white solid of which only a trace amount was not sublimable. Trimethylamine-chlorodifluoroborane (0.7279 g, 5.077 mmol, a yield of 89% based on

the amount of $(CH_3)_3NBHF_2$) was sublimed at room temperature in vacuo onto a dry ice/acetone cold finger.

Trimethylamine-chlorodifluoroborane, $(CH_3)_3NClF_2$, is a white crystalline solid, mp 136-137°. Anal. Calcd. for $(CH_3)_3NClF_2$: C, 25.31; H, 6.33; N, 9.77; F, 26.50; Cl, 24.73. Found: C, 25.04; H, 6.22; N, 9.66; F, 26.27; Cl, 24.49.

The infrared spectrum of $(CH_3)_3NBClF_2$ is described in Table 3-1 and shown in Figure 3-11.

The ^{11}B nmr spectrum as shown in Figure 3-12 consisted of a triplet of intensity 1:2:1 centered at 13.3 ppm upfield from $B(OCH_3)_3$ with J_{BF} = 43 Hz as the observed coupling constant.

The ^{19}F nmr spectrum as shown in Figure 3-13 consisted of a quartet of intensity 1:1:1:1 centered at 22.6 ppm downfield from C_6F_6 with J_{11BF} = 43 Hz and J_{10BF} = 14 Hz.

Reaction of trimethylamine-trifluoroborane and gaseous hydrogen chloride.-- Trimethylamine-trifluoroborane, $(CH_3)_3NBF_3$ (0.2349 g, 1.850 mmol), was dissolved in 75 ml of CH_2Cl_2 contained in a 4 oz polyethylene bottle. Hydrogen chloride was then passed. After 30 minutes, the nmr spectrum of the solution showed no change from the spectrum of the starting solution. The bottle was capped and allowed to remain at room temperature for three days. An nmr spectrum of this solution showed again only $(CH_3)_3NBF_3$ with no indication of $(CH_3)_3NBClF_2$ as a possible product. Hydrogen chloride was passed through the solution for another 30 minutes with the nmr spectrum remaining unchanged. The final nmr spectrum of the solution

after it had remained in the reaction bottle another three days indicated only $(CH_3)_3NBF_3$ and HCl.

After removal of solvent by nitrogen and sublimation, 0.1894 g, 81%, of the starting $(CH_3)_3NBF_3$ was recovered.

Reaction of trimethylamine-chlorofluoroborane and hydrogen chloride.-- A small amount of $(CH_3)_3NBHClF$ was dissolved in 1.5 ml of CH_2Cl_2 in an nmr tube. The nmr spectrum of this solution gave an intense peak at 156 Hz. Hydrogen chloride was then bubbled through this solution at a moderate rate using a long disposable pipet. After 10 minutes of HCl flow, the nmr spectrum showed no new peak. The solution was transferred to a 2-neck 50 ml flask containing 10 ml of CH_2Cl_2 saturated with HCl. Hydrogen chloride was passed through this solution for approximately 80 minutes. During this time nmr spectra of the solution sampled at intervals showed only the peak at 156 Hz due to the starting material, $(CH_3)_3NBHClF$.

Synthesis of trimethylamine-dichlorofluoroborane.-- Trimethylamine-chlorofluoroborane, $(CH_3)_3NBHClF$ (0.4238 g, 3.380 mmol), was dissolved in 50 ml of dry CH_2Cl_2 contained in a 100 ml 2-neck flask fitted with a gas inlet tube and drying tube filled with Drierite. Chlorine was passed through the solution with stirring at a moderate rate for approximately 20 minutes until a faint but persistent yellow coloration of the solution was achieved. The nmr spectrum of this solution showed no starting material but a sharp quartet at 170 Hz indicating a trihalogenated amine-borane. The following equation describes the reaction which had taken place.

$$(CH_3)_3NBHClF + Cl_2 \rightarrow (CH_3)_3NBCl_2F + HCl \qquad (3\text{-}6)$$

The white solid which remained after evaporating the solvent by the passage of nitrogen was transferred to a large sublimator. The sublimator was placed in a 60° oil bath and the trimethylamine-dichlorofluoroborane, $(CH_3)_3NBCl_2F$ (0.5040 g, 3.128 mmol; a 92% yield), was sublimed in vacuo onto the dry ice/acetone cold finger.

Trimethylamine-dichlorofluoroborane was also synthesized using $(CH_3)_3NBH_2F$ as the starting material. Chlorine was passed through a CH_2Cl_2 solution of $(CH_3)_3NBH_2F$ (0.3310 g, 3.640 mmol) until a permanent faint yellow color was achieved. After a few minutes of Cl_2 through the solution an nmr spectrum of the clear colorless solution indicated a peak at 152 Hz due to the starting material, $(CH_3)_3NBH_2F$, a peak at 156 Hz due to $(CH_3)_3NBHClF$ and a quartet at 170 Hz due to the desired product of the reaction, $(CH_3)_3NBCl_2F$. The spectrum of the final, yellow solution indicated $(CH_3)_3NBCl_2F$ as the only amine-borane. After evaporating the solution to dryness with nitrogen, the $(CH_3)_3NBCl_2F$ (0.4850 g, 3.035 mmol; a yield of 83%) was collected by sublimation as described above.

Trimethylamine-dichlorofluoroborane, $(CH_3)_3NBCl_2F$, is a white crystalline solid, mp 197°. Anal. Calcd. for $(CH_3)_3NBCl_2F$: C, 22.55; H, 5.68; N, 8.76; Cl, 44.36; F, 11.89. Found: C, 22.71; H, 5.56; N, 8.59; Cl, 44.45; F, 11.72.

The infrared spectrum of $(CH_3)_3NBCl_2F$ is described in Table 3-1 and shown in Figure 3-14.

The ^{11}B nmr spectrum as shown in Figure 3-15 consisted of a

doublet centered at 10.2 ppm upfield from $B(OCH_3)_3$ with J_{BF} = 68 Hz as the observed coupling constant.

The ^{19}F nmr spectrum as shown in Figure 3-16 consisted of a quartet of intensity 1:1:1:1 centered at 33.5 ppm downfield from C_6F_6 with J_{11BF} = 69 Hz and J_{10BF} = 23 Hz as the observed coupling constants.

Reaction of trimethylamine-trichloroborane and anhydrous hydrogen fluoride.-- Trimethylamine-trichloroborane, $(CH_3)_3NBCl_3$ (2.3598 g, 13.44 mmol), was dissolved in 175 ml of CH_2Cl_2 contained in an 8 oz polyethylene bottle. The nmr spectrum of this starting solution showed only a quartet centered at 179 Hz. Hydrogen fluoride was allowed to pass through the solution at a rather fast rate (35 bubbles/15 seconds) for 15 minutes. The nmr spectrum of this solution showed no change from the initial spectrum. However, after 40 minutes of HF flow, the spectrum showed the characteristic peak of $(CH_3)_3NBF_3$ at 157 Hz. This was the only peak in addition to that of the starting material at 179 Hz. After 2 hours of HF flow there was no further change in the nmr spectrum. It consisted only of the peak at 157 Hz due to $(CH_3)_3NBF_3$. As indicated by the absence of the quartet at 179 Hz, no starting material remained. After evaporating the solution to dryness, the $(CH_3)_3NBF_3$ was sublimed at room temperature in vacuo onto a dry ice/acetone cold finger. A 91% yield of $(CH_3)_3NBF_3$ (1.5455 g, 12.17 mmol) based on the amount of $(CH_3)_3NBCl_3$ was collected.

Trimethylamine-bromofluoroboranes

Synthesis of trimethylamine-bromofluoroborane.-- Trimethylamine-fluoroborane, $(CH_3)_3NBH_2F$ (0.1901 g, 2.094 mmol), was dissolved in 25 ml of dry CH_2Cl_2 contained in a 50 ml 2-neck flask that was fitted with a gas inlet tube and drying tube. Nitrogen was slowly passed through the solution for about 10 minutes before starting the hydrogen bromide, HBr, flow. There was an immediate vigorous gas evolution as HBr entered the solution. The reaction which was expected to occur, according to the following equation,

$$(CH_3)_3NBH_2F + HBr \rightarrow (CH_3)_3NBHBrF + H_2 \qquad (3\text{-}7)$$

was complete in less than 10 minutes with no further gas evolution or change in the nmr spectrum. When the bubbling had ceased, the nmr spectrum showed the absence of any starting material and a new peak at 161 Hz due to $(CH_3)_3NBHBrF$.

The solution was evaporated to dryness with nitrogen. The flask was then taken into a dry box where the white solid was transferred to a small sublimator. Trimethylamine-bromofluoroborane was handled in a dry box since it proved to be sensitive to moisture, forming an ammonium salt. It was then sublimed in vacuo from the ammonium salt which formed during the reaction onto a dry ice/acetone cold finger with the sublimator placed in a 40° oil bath. Trimethylamine-bromofluoroborane, $(CH_3)_3NBHBrF$, was collected in a yield of 72% (0.2550 g, 1.501 mmol) based on the amount of $(CH_3)_3NBH_2F$.

In one preparation the starting material contained a small

amount of $(CH_3)_3NBHF_2$. At the end of the reaction, it was separated from the product by fractional sublimation. Trimethylamine-difluoroborane was easily removed as the first fraction since it sublimed quickly in vacuo at room temperature.

Trimethylamine-bromofluoroborane, $(CH_3)_3NBHBrF$, is a white crystalline solid, mp 74-75°. Anal. Calcd. for $(CH_3)_3NBHBrF$: C, 21.23; H, 5.96; N, 8.28; F, 11.14; Br, 47.08. Found: C, 21.29; H, 6.12; N, 8.30; F, 11.36; Br, 46.84.

The infrared spectrum is described in Table 3-1 and shown in Figure 3-17. The B-H stretch for this compound is clearly indicated as a singlet at 2440 cm^{-1}.

The ^{11}B nmr spectrum as shown in Figure 3-18 consisted of a quartet of intensity 1:1:1:1 and centered at 13.3 ppm upfield from $B(OCH_3)_3$ with J_{BF} = 88 Hz and J_{BH} = 160 Hz as the observed coupling constants.

The ^{19}F nmr spectrum as shown in Figure 3-19 consisted of 8 peaks of equal intensity centered at 5.2 ppm downfield from C_6F_6 with J_{BF} = 88 Hz and J_{HBF} = 50 Hz as the observed coupling constants.

Synthesis of trimethylamine-dibromofluoroborane.-- Trimethylamine-monofluoroborane, $(CH_3)_3NBH_2F$ (0.2841 g, 3.124 mmol), along with a CH_2Cl_2 solution of bromine, Br_2 (0.03664 mole Br_2/25 ml of dry CH_2Cl_2) was taken into a dry box. The $(CH_3)_3NBH_2F$ was dissolved in 10 ml of dry CH_2Cl_2 and the Br_2 solution was added dropwise until there was no further gas evolution or discoloration of the Br_2 solution. Within a drop or two, 3.2 ml of the Br_2 solution was

added which was the amount calculated for complete reaction based on the overall stoichiometry for the reaction which was expected to occur according to the following equation.

$$(CH_3)_3NBH_2F + 3/2\ Br_2 \rightarrow (CH_3)_3NBBr_2F + HBr + 1/2\ H_2 \qquad (3\text{-}8)$$

When approximately half of the calculated amount of Br_2 solution had been added, an nmr of the clear colorless solution showed a new peak at 174 Hz, a quartet due to $(CH_3)_3NBr_2F$, along with a peak at 161 Hz due to $(CH_3)_3NBHBrF$ and the starting material peak at 152 Hz for $(CH_3)_3NBH_2F$. After the last drops of Br_2 solution had been added as indicated by the solution becomming a faint yellow, the nmr spectrum showed only a quartet at 174 Hz with a J_{HCNB} = 2.9 Hz as the observed coupling constant.

After removal of solvent the white solid was purified by sublimation in vacuo onto a dry ice/acetone cold finger with an oil bath at 80° surrounding the sublimator. The yield of $(CH_3)_3NBBr_2F$ was 76% (0.583 g, 2.343 mmol) based on the amount of $(CH_3)_3NBH_2F$.

Trimethylamine-dibromofluoroborane is a white crystalline solid, mp 152-153°. Anal. Calcd. for $(CH_3)_3NBBr_2F$: C, 14.49; H, 3.65; N, 5.63; F, 7.64; Br, 64.25. Found: C, 14.25; H, 3.75; N, 5.57; F, 7.46; Br, 64.03.

The infrared spectrum is described in Table 3-1 and shown in Figure 3-20.

The ^{11}B nmr spectrum as shown in Figure 3-21 consisted of a doublet centered at 15.2 (15.7) ppm upfield from $B(OCH_3)_3$ with

J_{BF} = 86 Hz as the observed coupling constant.

The ^{19}F nmr spectrum as shown in Figure 3-22 consisted of a quartet of 1:1:1:1 intensity centered at 45.0 ppm downfield from C_6F_6 with J_{BF} = 89 Hz.

Synthesis of trimethylamine-bromodifluoroborane.-- Trimethylamine-difluoroborane, $(CH_3)_3NBHF_2$ (0.2112 g, 1.942 mmol), which had been freshly sublimed was taken into a dry box along with a CH_2Cl_2 solution of Br_2 (0.03664 mole Br_2/25 ml of dry CH_2Cl_2). The $(CH_3)_3NBHF_2$ was dissolved in 10 ml of dry CH_2Cl_2 and Br_2 solution was added dropwise and was immediately discolored. The reaction was expected to occur according to the following equation.

$$(CH_3)_3NBHF_2 + Br_2 \rightarrow (CH_3)_3NBBrF_2 + HBr \qquad (3\text{-}9)$$

According to the stoichiometry of this equation, the amount of Br_2 solution that was calculated as necessary for complete reaction was 1.32 ml. After the addition of 1.3 ml of Br_2 solution, the reaction mixture became a faint yellow. The nmr spectrum of the final reaction solution showed a somewhat broadened quartet centered at 164 Hz.

After removal of the solvent, the white solid was purified by sublimation. With the sublimator placed in an oil bath at 40°, $(CH_3)_3NBBrF_2$ was readily sublimed in vacuo onto a dry ice/acetone cold finger.

It was of interest to note the difference in volatility of $(CH_3)_3NBBrF_2$ as compared to $(CH_3)_3NBBr_2F$. This difference was useful in a preparation of $(CH_3)_3NBBr_2F$. In this preparation,

$(CH_3)_3NBHF_2$ was present as an impurity in the starting material. After bromination, it became an impurity in the product as $(CH_3)_3NBBrF_2$. However, since $(CH_3)_3NBBrF_2$ has a higher volatility than the product, $(CH_3)_3NBBr_2F$, it was removed by fractional sublimation. Trimethylamine-bromodifluoroborane was collected as the fraction which sublimed in vacuo at 40°. The sublimation procedure was then continued in vacuo but at 80° to collect the desired product, $(CH_3)_3NBBr_2F$.

Trimethylamine-bromodifluoroborane, $(CH_3)_3NBBrF_2$, is a white crystalline solid, mp 110°. Anal. Calcd. for $(CH_3)_3NBBrF_2$: C, 19.18; H, 4.83; N, 7.51; F, 20.23; Br, 42.57. Found: C, 19.24; H, 4.96; N, 7.59; F, 20.03; Br, 42.37.

The infrared spectrum is described in Table 3-1 and shown in Figure 3-23.

The ^{11}B nmr spectrum as shown in Figure 3-24 consisted of a triplet of intensity of 1:2:1 centered at 14.1 ppm upfield from $B(OCH_3)_3$ with J_{BF} = 54 Hz as the observed coupling constant.

The ^{19}F nmr spectrum as shown in Figure 3-25 consisted of a 1:1:1:1 quartet centered at 31.7 ppm downfield from C_6F_6 with J_{BF} = 54 Hz as the observed coupling constant.

Synthesis of trimethylamine-bromochlorofluoroborane.-- Trimethylamine-chlorofluoroborane, $(CH_3)_3NHClF$ (0.1866 g, 1.481 mmol), was taken into a dry box along with a freshly prepared Br_2 solution (0.01832 mole Br_2/25 ml of dry CH_2Cl_2) and dissolved in 5 ml of dry CH_2Cl_2. The reaction was expected to occur according to the

following equation.

$$(CH_3)_3NBHClF + Br_2 \rightarrow (CH_3)_3NBBrClF + HBr \qquad (3\text{-}10)$$

According to the stoichiometry of this reaction, 2.02 ml of Br_2 was calculated as the required amount. This amount of the Br_2 solution was added dropwise with an extra drop finally imparting a faint yellow color.

The ^1H nmr spectrum of this solution showed a clean quartet at 173 Hz with J_{HCNB} = 2.5 Hz.

After removal of the solvent, the white solid was purified by sublimation at 90° in vacuo onto a dry ice/acetone cold finger.

Trimethylamine-bromochlorofluoroborane, $(CH_3)_3NBBrClF$, is a white crystalline solid, mp 165°. Anal. Calcd. for $(CH_3)_3NBBrClF$: C, 17.64; H, 4.44; N, 6.86; Br, 39.12; Cl, 17.35; F, 9.30. Found: C, 17.48; H, 4.69; N, 6.62; Br, 38.90; Cl, 17.06; F, 9.60.

The infrared spectrum is described in Table 3-1 and shown in Figure 3-26.

The ^{11}B nmr spectrum as shown in Figure 3-27 consisted of a doublet centered at 12.0 ppm upfield from $B(OCH_3)_3$ with J_{BF} = 82 Hz as the observed coupling constant.

The ^{19}F nmr spectrum as shown in Figure 3-28 consisted of a 1:1:1:1 quartet centered at 39.3 ppm downfield from C_6F_6 with J_{BF} = 79 Hz as the observed coupling constant.

Reaction of trimethylamine-dibromochloroborane and anhydrous hydrogen fluoride.-- Trimethylamine-dibromochloroborane, $(CH_3)_3NBBr_2Cl$ (0.1616 g, 1.616 mmol), was dissolved in 35 ml of dry CH_2Cl_2 contained

in a 4 oz polyethylene bottle. The nmr spectrum of this solution showed only the expected quartet at 184 Hz. A stoichiometric amount (4.2 ml of 0.38 M) of a CH_2Cl_2 solution of HF was quickly added to the solution and the bottle was capped. With the nmr spectrum of the solution unchanged after several days, HF was passed through the solution. Samples (0.5 ml) of solution were removed for analysis by ^1H nmr at 10 minute intervals. The nmr spectrum remained unchanged for the first two intervals, showing only the quartet at 184 Hz. However, after the third interval, the spectrum showed only a peak characteristic of $(CH_3)_3NBF_3$ at 157 Hz. No other boranes were observed during this process. The solution was evaporated to dryness with nitrogen and 0.1575 g, a 77% yield of $(CH_3)_3NBF_3$ based on the amount of $(CH_3)_3NBBr_2Cl$ was collected by sublimation in vacuo at room temperature.

Reaction of trimethylamine-bromoborane and anhydrous hydrogen fluoride.-- Trimethylamine-bromoborane, $(CH_3)_3NBH_2Br$ (0.2338g, 1.539 mmol), was dissolved in 80 ml of dry CH_2Cl_2 and the reaction bottle positioned in the HF apparatus. After 3 minutes of moderate HF flow an nmr spectrum of the solution showed no discernible changes from that of the starting solution which indicated only a peak at 163 Hz due to the $(CH_3)_3NBH_2Br$. After several more minutes of HF, a peak began developing at 161 Hz, the chemical shift for $(CH_3)_3NBHBrF$. As HF flow was continued subsequent spectra showed the appearance of peaks at 148 Hz and 157 Hz as the initial peak at 163 Hz disappeared. The peak at 148 Hz, indicative of

$(CH_3)_3NBHF_2$, was also lost from the spectrum. The final nmr spectrum of the reaction solution showed only a peak at 157 Hz which was a broad multiplet characteristic of $(CH_3)_3NBF_3$.

Reaction of trimethylamine-bromofluoroborane with trimethylamine.-- Trimethylamine-bromofluoroborane, $(CH_3)_3NBHBrF$, was freshly prepared by passing HBr through a benzene solution of $(CH_3)_3NBH_2F$ (0.1567 mmol in 25 ml of dry benzene) which was contained in a 3-neck 50 ml flask. The flask was fitted with a gas inlet tube, rubber septum, and drying tube filled with Drierite. After a few minutes of HBr passage, gas evolution ceased indicating that monobromination was complete. Hydrogen bromide was then replaced by nitrogen to remove any excess HBr from the system. A ^1H nmr spectrum of this solution showed only a peak at 112 Hz for $(CH_3)_3NBHBrF$. Trimethylamine, $(CH_3)_3N$, was then passed through the solution at a moderate rate for 15 minutes. A small amount of white solid precipitated from solution. The nmr spectrum of this solution showed the presence of a large amount of $(CH_3)_3N$ as the only change from the prior spectrum. The passage of $(CH_3)_3N$ was discontinued and the solution remained overnight at room temperature. Subsequent nmr spectra showed no indication of possible cation formation. At these conditions there appeared to be no reaction between $(CH_3)_3N$ and $(CH_3)_3NBHBrF$.

Trimethylamine-fluoroiodoboranes

Reaction of trimethylamine-iodoborane and anhydrous hydrogen

fluoride.-- A portion (40.0 ml) of a freshly prepared CH_2Cl_2 solution of trimethylamine-iodoborane, $(CH_3)_3NBH_2I$ (13.0 mmol), was transferred to a small polyethylene bottle containing 50 ml of dry CH_2Cl_2 and a magnetic stirring bar. The reaction bottle was positioned in the HF aparatus and a slow, moderate flow of HF was begun through the solution. After a few minutes of HF passage an nmr spectrum showed that a slight amount of $(CH_3)_3NBHF_2$ had formed as indicated by the peak at 148 Hz. Continued addition of HF caused an increase in this peak and also the appearance of the peak characteristic of $(CH_3)_3NBF_3$ at 157 Hz. After approximately 40 minutes of HF flow the nmr spectrum indicated only $(CH_3)_3NBF_3$. It should be noted that no peak at 152 Hz, indicative of $(CH_3)_3NBH_2F$ was observed in the sequence of nmr spectra. The HF flow was replaced by nitrogen and the solution allowed to evaporate to dryness. The white solid which remained was transferred to a sublimator from which 1.3944 g, 10.9 mmol of $(CH_3)_3NBF_3$ was collected.

Reaction of trimethylamine-iodoborane and a methylene chloride solution of hydrogen fluoride.-- Trimethylamine-iodoborane, $(CH_3)_3NBH_2I$, was also allowed to react with a freshly prepared CH_2Cl_2 solution of HF in an amount slightly in excess of a 1:1 stoichiometry. The CH_2Cl_2 solution (22.9 ml) of HF (0.60 M) was added to dry CH_2Cl_2 containing 13.8 mmol of $(CH_3)_3NBH_2I$. The nmr spectrum did not change from that of the starting solution of $(CH_3)_3NBH_2I$ even though the reaction solution was allowed to remain overnight. Only on passing HF through the solution did reaction

occur and then as described above to produce $(CH_3)_3NBF_3$.

Reaction of trimethylamine-fluoroborane and iodine.-- Trimethylamine-fluoroborane, $(CH_3)_3NBH_2F$ (0.1853 g, 2.037 mmol), and 0.4176 g of iodine, I_2, were taken into a dry box. The $(CH_3)_3NBH_2F$ was dissolved in 10 ml of dry CH_2Cl_2. Upon initial piecewise addition of I_2, the solution remained colorless as the I_2 was consumed with gas evolution. Reaction was expected to occur according to the following equation.

$$(CH_3)_3NBH_2F + I_2 \longrightarrow (CH_3)_3NBHIF + HI \qquad (3\text{-}11)$$

After approximately one-fourth to one-third of the stoichiometric amount of I_2 had been added, the solution became and remained an intense red-brown color. The nmr spectrum of the solution after it had remained overnight indicated the products to be $(CH_3)_3NBH_2I$ at 169 Hz and $(CH_3)_3NBF_3$ at 157 Hz.

This reaction was repeated with trimethylamine, di-isopropylamine, 2,4,6-tri-tertbutylamine, or cyclohexene added initially in approximately a 10% excess over a 1:1 molar ratio with $(CH_3)_3NBH_2F$. The presence of any one of these species in the reaction mixture did not affect the reaction. The final nmr spectra of the solutions of these reaction mixtures also showed peaks at 157 Hz and 169 Hz indicating, again, the products to be $(CH_3)_3NBF_3$ and $(CH_3)_3NBH_2I$ respectively.

Reaction of trimethylamine-fluoroborane and hydrogen iodide.-- Trimethylamine-fluoroborane, $(CH_3)_3NBH_2F$ (0.2276 g, 2.502 mmol), was dissolved in 25 ml of dry CH_2Cl_2 contained in a 50 ml 3-neck flask that was fitted with a gas inlet tube, rubber septum, and

drying tube filled with Drierite. The passage of either hydrogen iodide, HI, or nitrogen was facilitated by means of a Y-connection to the gas inlet tube. After only a short exposure, approximately 15 seconds, of the solution to HI during which there was gas evolution, the gas inlet tube was switched to nitrogen flow. The nmr spectrum of this solution showed new peaks at 169 Hz, 166 Hz, and 148 Hz, of which the peak at 169 Hz was attributed to $(CH_3)_3NBH_2I$ and the peak at 148 Hz was attributed to $(CH_3)_3NBHF_2$ on the basis of previous reactions and spectra. Nitrogen and HI were passed alternately through the solution with intermittant standing until there was no further change in the nmr spectrum. The final nmr spectrum was taken after the solution had remained overnight. The peak at 166 Hz decreased after its initial appearance and finally disappeared from the spectrum. A peak at 157 Hz characteristic of $(CH_3)_3NBF_3$ appeared in the spectrum as the peak at 148 Hz disappeared from the spectrum. In the final solution, the peak at 157 Hz was identified as $(CH_3)_3NBF_3$, and the peak at 169 Hz was identifed as $(CH_3)_3NBH_2I$. A doublet seemingly interfering with the sharpness of the peak at 169 Hz and attributable to ammonium salt was also observed in the spectrum. A small broad peak at 182 Hz remained unidentified.

Reaction of trimethylamine-fluoroborane and a methylene chloride solution of hydrogen iodide.-- Trimethylamine-fluoroborane, $(CH_3)_3NBH_2F$ (0.4783 g, 5.259 mmol), was dissolved in 7 ml of dry CH_2Cl_2 and this solution was transferred to a pressure-equalizing

funnel along with the two small portions of CH_2Cl_2 used to rinse the beaker so that the funnel contained 10 ml of $(CH_3)_3NBH_2F$ solution. A CH_2Cl_2 solution of HI was prepared by passing HI through a drying tube filled with KI into 150 ml of CH_2Cl_2 for approximately 10 minutes or until the solution was a faint violet. The solution was then titrated with 1.0 M NaOH and phenothalein as an indicator. A portion (40.0 ml) of the freshly prepared CH_2Cl_2 solution of HI (0.12 M) was quickly added to a 100 ml 3-neck flask containing a stirring bar and fitted with the pressure-equalizing funnel and drying tube of Drierite. A rubber septum was quickly positioned in the third neck of the flask and with stirring a fast dropwise addition of the $(CH_3)_3NBH_2F$ was begun. There was an immdediate yellowing of the solution and a rapid gas evolution. The $(CH_3)_3NBH_2F$ solution was added with only a brief pause so that the entire addition was complete in 5 minutes. The nmr spectrum of a 0.5 ml sample of this solution showed mainly a peak at 166 Hz but with a slight shoulder at 169 Hz and a very small peak at 148 Hz due to $(CH_3)_3NBH_2F$, but which could easily have been part of the starting material rather than a product of the reaction.

It was not possible to isolate for elemental analysis the species responsible for the peak at 169 Hz in this reaction mixture but evidence strongly suggested it to be $(CH_3)_3NBHIF$. Its appearance in the ^1H nmr at 166 Hz, 3 cycles upfield from $(CH_3)_3NBH_2I$, followed the same pattern of a 2 or 3 cycle upfield shift for other monofluoroderivatives of trimethylamine-monohalo-

boranes. Examples of this pattern were seen in the ^{1}H nmr data for $(CH_3)_3NBHClF$ (156 Hz) and $(CH_3)_3NBHBrF$ (161 Hz) as compared respectively to $(CH_3)_3NBH_2Cl$ (158 Hz) and $(CH_3)_3NBH_2Br$ (163 Hz). The most intense resonance in the ^{19}F nmr spectrum as shown in Figure 3-29 consisted of an equal intensity octet centered at 10.3 ppm downfield from C_6F_6. This new chemical shift in the ^{19}F spectrum was reasonable compared to the data for $(CH_3)_3NBHClF$ (0.9 ppm downfield) and $(CH_3)_3NBHBrF$ (5.2 ppm downfield). The overall appearance of an equal intensity octet in the ^{19}F spectrum supported the stoichiometry of $(CH_3)_3NBHIF$. The multiplicity of the peak was accounted for as a 1:1:1:1 quartet, resulting from the spin coupling of the ^{19}F nucleus with the ^{11}B nucleus, with each peak of the quartet split into a 1:1 doublet by the spin coupling of the ^{19}F nucleus with the ^{1}H nucleus. The observed coupling constants in the ^{19}F spectrum were J_{BF} = 94 Hz and J_{HBF} = 48 Hz. The ^{11}B spectrum as shown in Fiture 3-30 was also reasonable for the assignment of $(CH_3)_3NBHIF$. The main resonance in the ^{11}B spectrum for this reaction mixture consisted of a 1:1:1:1 quartet centered at 16.1 ppm upfield from $B(OCH_3)_3$ with J_{BH} = 168 Hz and J_{BF} = 92 Hz as the observed coupling constants. The ^{11}B chemical shifts for $(CH_3)_3NBHClF$ and $(CH_3)_3NBHBrF$ were 12.1 ppm and 13.3 ppm upfield respectively. The multiplicity and intensity of the ^{11}B resonance were also accounted for by the stoichiometry of $(CH_3)_3NBHIF$. A 1:1 doublet resulted from the spin coupling of the ^{11}B nucleus with the ^{19}F nucleus. Each of

these peaks was further split by the spin coupling of the ^1H nucleus thereby giving a 1:1:1:1 quartet as the observed spectrum.

The ^1H spectrum of a CH_2Cl_2 solution of principally $(CH_3)_3NBHIF$ which remained at room temperature for 12-15 hours showed a marked decrease in the intensity of the peak at 166 Hz and the appearance of peaks at 157 Hz, 169 Hz, and 182 Hz which were assigned as $(CH_3)_3NBF_3$, $(CH_3)_3NBH_2I$, and $(CH_3)_3NBHI_2$ respectively on the basis of previous spectra.

Attempts to isolate $(CH_3)_3NBHIF$ by fractional sublimation also resulted in a mixture of $(CH_3)_3NBF_3$, $(CH_3)_3NBH_2I$, and $(CH_3)_3NBHI_2$. The sublimator for this procedure was evacuated and positioned in an oil bath at 45°. The cold finger of the sublimator was filled with a dry ice/acetone mixture.

Reaction of the trimethylamine-fluoroiodoborane solution with a methylene chloride solution of hydrogen fluoride.-- A portion (5.0 ml) of the above freshly prepared $(CH_3)_3NBHIF$ solution (approximately 0.6 mmol) was transferred by syringe into a small polyethylene bottle containing 2.0 ml of freshly titrated CH_2Cl_2 solution of HF (0.14 M). The 2.0 ml of HF solution provided a 0.084 mmol excess of HF as a 1:1 stoichiometry required 1.4 ml of the HF solution. Immediately upon mixing a ^1H nmr spectrum was taken. This spectrum showed that no starting material remained but that the peak present in largest amount was at 148 Hz and was due to $(CH_3)_3NBHF_2$. Trimethylamine-trifluoroborane was also present but in a smaller amount. The other feature of the spectrum could have

been considered as either a quartet at 170 Hz or a broadened doublet at 169 and 172 Hz. Hartman and Miller have observed a quartet at 165 Hz for $(CH_3)_3NBIF_2$ in a mixture of fluoroiodoboranes of trimethylamine.[5]

Another 5.0 ml portion of the $(CH_3)_3NBHIF$ solution prepared as above was syringed into a small polyethylene bottle containing approximately five times the amount of HF solution required for stoichiometry. The nmr spectrum of this solution immediately after mixing indicated only $(CH_3)_3NBHF_2$ besides a small broad rise in the baseline centered at 170 Hz. After the solution had remained at room temperature for 2 hours with the polyethylene bottle capped, the nmr spectrum of a 0.5 ml sample showed that the $(CH_3)_3NBHF_2$ had been converted to $(CH_3)_3NBF_3$. The rest of the spectrum was unchanged.

Reaction of the trimethylamine-fluoroiodoborane solution with a methylene chloride solution of hydrogen iodide.-- A 4.0 ml portion of freshly prepared CH_2Cl_2 solution of HI (0.14 M) was placed in a 25 ml round-bottom flask fitted with a rubber septum. A 5.0 ml portion of the $(CH_3)_3NBHIF$ solution prepared above was added to the HI solution by syringe. An immediate nmr spectrum indicated only a small decrease in the intensity of the peak at 166 Hz with the appearance of small equal amounts of $(CH_3)_3NBHF_2$ and $(CH_3)_3NBF_3$. There was also a rather sharp peak at 169 Hz. After the solution had remained overnight, the nmr spectrum of a 0.5 ml sample showed no $(CH_3)_3NBHIF$ but only $(CH_3)_3NBF_3$ with

just a small amount of $(CH_3)_3NBHF_2$.

The other feature of the spectrum was an intense and sharp doublet at 169 and 172 Hz characteristic of and ammonium salt.

Reaction of the trimethylamine-fluoroiodoborane solution with bis-triphenylphosphineiminium chloride.-- A 5.0 portion of the $(CH_3)_3NBHIF$ solution prepared above and containing approximately 0.50 mmol of $(CH_3)_3NBHIF$ was transferred by syringe to a 2-neck 50 ml flask fitted with rupper septum and drying tube of Drierite. The flask contained approximately 0.50 mmol of $((C_6H_5)_3P)_2NCl$ in several ml of dry CH_2Cl_2. After the solution had stirred briefly, a 0.5 ml sample was removed for analysis by ^1H nmr. The spectrum showed a peak at 156 Hz as previously seen for $(CH_3)_3NBHClF$ and the small doublet at 169 and 172 Hz characteristic of an ammonium salt. The solution was evaporated to dryness with nitrogen and the solid which remained was transferred to a sublimator. The sublimator was placed in an oil bath at 40^0 and a white solid sublimed in vacuo onto a dry ice/acetone cold finger. The infrared spectrum and melting point of this compound were identical to those previously observed for $(CH_3)_3NBHClF$.

Reaction of the trimethylamine-fluoroiodoborane solution with trimethylamine.-- Two 5.0 ml portions of the $(CH_3)_3NBHIF$ reaction solution were syringed into a 50 ml 2-neck flask with gas inlet and drying tube. Nitrogen was passed through the solution for a few minutes to rid the system of any HI. The nitrogen was then replaced by a moderate flow of trimethylamine, $(CH_3)_3N$. On contact

with $(CH_3)_3N$ the solution lost its yellow color and a small amount of a white solid precipitated. When the nmr spectrum showed the complete disappearance of the major peak at 166 Hz assigned to $(CH_3)_3NBHIF$ and the smaller peak at 169 Hz assigned to $(CH_3)_3NBH_2I$, the solution was evaporated to dryness with nitrogen. The white solid which remained was dissolved in water. On addition of a saturated ammonium hexafluorophosphate, a white solid precipitated from the solution. This white solid was presumably the hexafluorophosphate salt of the cations, $((CH_3)_3N)_2BHF^+$ and $((CH_3)_3N)_2BH_2^+$ which had formed on passing $(CH_3)_3N$ through the solution. On recrystallization from hot water, a white solid, mp 147°, was obtained. From the observation of this reaction and the nmr spectrum, this white solid was considered to be mostly $((CH_3)_3N)_2BHF^+PF_6^-$ but to also contain a small amount of $((CH_3)_3N)_2BH_2^+PF_6^-$. Muetterties[17] has noted that on monofluorination of $((CH_3)_3N)_2BH_2^+PF_6^-$, the infrared spectrum indicated the collapse of the B-H doublet to a weak singlet (with shoulder), the complete disappearance of the band at 1000 cm^{-1} and the appearance of a rather symmetrical triplet centered at 1180 cm^{-1}. The infrared spectrum of the salt obtained in this reaction is in agreement with such a comparative description. The infrared spectra are shown for comparison in Figure 3-31 and Figure 3-32. Muetterties reported $((CH_3)_3N)_2BH_2^+PF_6^-$ to be a white solid, mp 159°.

Reaction of trimethylamine-iodoborane and hydrogen chloride.-- A portion (40.0 ml) of a freshly prepared CH_2Cl_2 solution of tri-

methylamine-iodoborane, $(CH_3)_3NBH_2I$ (14.9 mmol), was diluted with 40 ml of dry CH_2Cl_2 in a polyethylene bottle and positioned for passage of HCl. After 30 minutes of HCl flow (2 bubbles/second) the nmr spectrum of a removed sample showed an incipient peak at 159 Hz attributable to $(CH_3)_3NBH_2Cl$. This peak increased only slightly during another 90 minutes of HCl flow. At this point HCl flow was discontinued, the bottle was capped, and the solution was allowed to remain overnight. Hydrogen chloride passage was resumed for 5 hours the following day with only a slight increase in the amount of $(CH_3)_3NBH_2Cl$. Even at these forcing conditions, HCl reacts with $(CH_3)_3NBH_2I$ only to a very small extent.

Reaction of hydrogen halides with trimethylamine borane.-- A series of reactions involving two competing hydrogen halides for $(CH_3)_3NBH_3$ were done to obtain a qualitative comparison of their relative rates of reaction with the $(CH_3)_3NBH_3$ in a solution of dry CH_2Cl_2. An amount of known concentration of $(CH_3)_3NBH_3$ solution was added to a polyethylene bottle containing freshly prepared and titrated solutions of two hydrogen halides. Samples of the reaction solution were removed at intervals for analysis by ^1H nmr. The results of such reactions are shown in Table 3-2. Qualitatively, the relative rate of reaction of HX towards $(CH_3)_3NBH_3$ as observed in the reactions and shown by the data in Table 3-1 is as follows:

$$HI > HBr \gg HF > HCl$$

Reaction of triethylamine-borane and anhydrous hydrogen fluoride.-- A drop of triethylamine-borane, $(C_2H_5)_3NBH_3$, was added

to an nmr tube containing 1.0 ml of dry CH_2Cl_2. The nmr spectrum of this solution showed the quartet and triplet of the ethyl group to be at 165 Hz and 69 Hz respectively. The content of the nmr tube was transferred to a small polyethylene bottle for the passage of HF and a 2 ml portion of dry CH_2Cl_2 was added to the bottle. There was an immediate and vigorous gas evolution as HF came in contact with the solution. The HF flow was continued for about 1 minute and then a 0.5 ml sample was removed for analysis by ^1H nmr.

Only the methylene resonance for the ethyl group will be reported in the description of the nmr spectra since it was the one used to interpret the spectra and monitor the progress of the reaction. The methyl resonance was not used since for a mixture of these compounds it consisted of overlapping triplets which could not be easily distinguished.

The nmr spectrum of the above solution showed that the peak due to the starting material had almost disappeared and that two new quartets of equal intensity had appeared at 168 Hz and 188 Hz. These peaks were considered as possibly attributable to $(C_2H_5)_3NBH_2F$ and $(C_2H_5)_3BHF_2$.

A vigorous gas evolution continued in the reaction bottle. After approximately 2 minutes of HF flow, the solution appeared to be two layers of liquid. The nmr spectrum of a sample of this solution showed no peak for the starting material, the complete disappearance of the quartet at 168 Hz, the almost complete disappearance of the quartet at 188 Hz and the appearance of a

new quartet at 176 Hz. Each peak of the quartet at 176 Hz had the characteristic multiplicity of the peak for $(CH_3)_3NBF_3$.

The above procedure was repeated on a larger scale using the polyethylene apparatus for the passage of HF. Again, gas evolution was immediate upon entry of HF into the solution. The reaction was monitored by observing the nmr spectra taken at intervals during the passage of HF. The quartet for the starting material at 165 Hz was quickly destroyed as the quartet at 169 Hz developed. Within 10 minutes, the quartet at 169 Hz attributed to possible $(C_2H_5)_3NBH_2F$ had almost disappeared and a new very sharp quartet had appeared further downfield at 192 Hz. Within the next few minutes, gas evolution slowly ceased. A ^1H nmr spectrum of this solution showed that a set of very sharp peaks at 189 Hz and 194 Hz had developed. The HF flow was continued but no further changes were observed. The doublet of quartets which had appeared persisted in the subsequent nmr spectra. It should be noted that no quartet with each peak having the multiplicity characteristic of trimethylamine-trifluoroborane developed as in the first small-scale reaction.

In another attempt to prepare triethylamine-difluoroborane, $(C_2H_5)_3NBHF_2$, 0.9495 g of triethylamine-borane, $(C_2H_5)_3NBH_3$, was dissolved in 125 ml of dry CH_2Cl_2 contained in an 8 oz polyethylene bottle. Gas evolution was immediate upon contact of HF with the solution. After approximately 1 minute of HF, an nmr spectrum of the solution showed that the quartet at 165 Hz

due to starting material had diminished to about one-half and a quartet of equal intensity appeared at 169 Hz. After 10 minutes of HF flow, the nmr spectrum of the solution showed no quartet at 165 Hz, but new closely spaced quartets at 189 Hz and 194 Hz in addition to the quartet at 169 Hz. After another 10 minutes of HF flow, gas evolution ceased. A ^1H nmr spectrum of this solution showed only the quartets at 189 Hz and 194 Hz which strongly suggested the presence of an ammonium salt. The solution was evaporated to dryness with nitrogen, leaving a white solid which was very hygroscopic. An infrared spectrum of this solid showed a strong band at 2700 cm^{-1} which indicated the presence of an N-H stretch, typical of ammonium salts. The spectrum also showed features which were identifyingly characteristic of BF_4^-, namely, a broad band at 1000 - 1200 cm^{-1} and a sharp doublet at 530 - 520 cm^{-1}.

Reaction of triethylamine-trifluoroborane and anhydrous hydrogen fluoride.-- A small amount of triethylamine-trifluoroborane, $(C_2H_5)_3NBF_3$, which had been prepared by condensing a slight excess of boron trifluoride, BF_3, onto triethylamine, $(C_2H_5)_3N$, was dissolved in dry CH_2Cl_2 in a polyethylene bottle. The reaction bottle was positioned for the passage of HF. Samples of the solution (0.5 ml) were removed at intervals for analysis by ^1H nmr. After HF had been passed for 25 minutes, the nmr spectrum showed no change from the spectrum of the starting solution. The polyethylene bottle was capped and it remained at room temperature overnight. It was observed that the ammonium salt of triethylamine-

boranes was more soluble in CH_2Cl_2 than the ammonium salt for the corresponding trimethylamine-boranes. However, an ammonium salt of trimethylamine-borane is sufficiently soluble in CH_2Cl_2 so that its presence in CH_2Cl_2 can be observed in a ^1H nmr spectrum. After the above solution had remained overnight, a ^1H nmr spectrum showed no indication of ammonium salt formation.

Reaction of trimethylamine-trifluoroborane and trimethylamine-borane.-- In order for this reaction to be done at elevated temperatures and in the absence of moisture, a glass tube was constructed that could be sealed off for the reaction and then opened to a vacuum line at the completion of the reaction. The length of glass tubing for a 24/40 female joint (20 cm) was closed and was constricted near the ground glass joint. A side arm which contained a break seal was joined to the tube about 5 cm down from the constriction. The side arm had an 18/7 socket joint for convenient attachment to a vacuum line. This piece of apparatus was dried in an oven for several hours and was cooled with nitrogen just prior to use in a dry box. In a dry box, it was charged with freshly sublimed $(CH_3)_3NBF_3$ and $(CH_3)_3NBH_3$ in a molar ratio of 2:1 (4.386 mmol $(CH_3)_3NBF_3$ and 2.1938 mmol of $(CH_3)_3NBH_3$). It was removed from the dry box, cooled to -196°, evacuated, and sealed off by a torch at the constriction. This glass reaction tube was then immersed in an oil bath for long term heating. The oil bath temperature was approximately 145° for 24 hours and then increased to 160° for 5 hours. After

cooling to room temperature overnight, the tube was attached to a vacuum line and checked for non-condensable. There was none. Cold traps at -78° and -196° were arranged to collect the volatile fractions. However, the volatile material was so slowly separated from the reaction mixture that the apparatus was removed from the vacuum line and was cracked open. A hard white solid was scraped out and a small amount of it was dissolved in CH_2Cl_2. The ^1H nmr spectrum of this solution was identical to the spectrum of the starting mixture with the exception of a small broad rise in the baseline on the upfield side of the symmetrical single peak at 157 Hz. The ^{11}B nmr spectrum for this solution also showed no peaks that could be assigned as $(CH_3)_3NBH_2F$ or as an appreciable amount of $(CH_3)_3NBHF_2$.

Thermal stability of trimethylamine-difluoroborane.-- A glass apparatus as previously described was taken into the dry box and was charged with freshly sublimed trimethylamine-difluoroborane, $(CH_3)_3NBHF_2$ (0.403 g, 3.70 mmol). On removal from the dry box, it was cooled to -196°, evacuated, and was submerged in an oil bath at 135° for 27 hours. At this temperature, the content of the tube was a clear liquid. The oil bath temperature was increased to 150° for 6 hours. After cooling to room temperature overnight, the tube was attached to a vacuum line and checked for non-condensable gas. There was none. The tube was opened in a dry box and a portion of the white solid was dissolved in CH_2Cl_2. A ^1H nmr spectrum of this solution showed a peak at 157 Hz without the characteristic multiplicity of $(CH_3)_3NBF_3$ and a small rise in the baseline at

148 Hz indicating that a slight amount of the starting material, $(CH_3)_3NBHF_2$, remained. This spectrum was identical in appearance to the spectrum of the sample of the 2:1 mixture of $(CH_3)_3NBF_3$ and $(CH_3)_3NBH_3$ which had been heated for a long time.

Two small tubes each designed with a constriction and a 18/7 socket joint were taken into a dry box and each charged with a small amount of freshly sublimed $(CH_3)_3NBHF_2$. The tubes were removed from the dry box, cooled to -196°, evacuated, and sealed off at the constriction. One of the tubes was immersed in the oil bath and heated for 12 hours at 105°. After cooling to room temperature, the tube was opened in the dry box and two solutions of the fused white solid were made for ^1H nmr analysis. The nmr spectrum of a CH_2Cl_2 solution of this solid showed only two peaks. The one small peak at 148 Hz was due to the starting material, $(CH_3)_3NBHF_2$. The large single peak at 157 Hz was presumably due to a mixture of $(CH_3)_3NBF_3$ and $(CH_3)_3NBH_3$. The nmr spectrum of a benzene solution of this solid showed three peaks. The small peak at 107 Hz was assigned to $(CH_3)_3NBHF_2$ on the basis of a known spectrum for this concentration of $(CH_3)_3NBHF_2$ in benzene. The peaks at 111 Hz and 122 Hz were found to be due to $(CH_3)_3NBF_3$ and $(CH_3)_3NBH_3$ respectively. The peak at 111 Hz had the multiplicity characteristic of $(CH_3)_3NBF_3$. Hence, for this series of experiments, benzene was found to be useful as a solvent since it differentiated the chemical shifts of $(CH_3)_3NBH_3$ and $(CH_3)_3NBF_3$.

The second sealed tube was heated in an oil bath for 6 hours

at 105° and for 12 hours at 120°. The nmr spectrum of a benzene solution of this white solid showed only two peaks at 110 Hz and 121 Hz. These peaks were assigned as $(CH_3)_3NBF_3$ and $(CH_3)_3BH_3$ respectively. Their ratio of 2:1 indicated the complete disproportionation of the $(CH_3)_3NBHF_2$ according to the following equation.

$$3\ (CH_3)_3NBHF_2 \rightarrow (CH_3)_3NBH_3 + 2\ (CH_3)_3NBF_3 \qquad (3\text{-}12)$$

Another sealed tube containing a small smount of freshly sublimed $(CH_3)_3NBHF_2$ was heated for 15 minutes at 127°, four degrees above its melting point. The nmr spectrum of a benzene solution of this solid after it had cooled to room temperature indicated the disproportionation of $(CH_3)_3NBHF_2$ was almost complete. The peak at 148 Hz due to $(CH_3)_3NBHF_2$ was very small. The two new peaks in the spectrum were at 110 Hz and 121 Hz in a ratio of 2:1 and were assigned to $(CH_3)_3NBF_3$ and $(CH_3)_3NBH_3$ respectively.

The stability of trimethylamine-difluoroborane was also investigated in benzene at reflux temperature, in benzene at room temperature, and in CH_2Cl_2 at room temperature. In a dry box, three nmr tubes, each fitted with an 18/7 socket joint and vacuum line adapter, were charged with a small amount of freshly sublimed $(CH_3)_3NBHF_2$. Dry benzene (0.5 ml) was added to two of the tubes and dry CH_2Cl_2 (0.5 ml) was added to the third tube. The tubes were removed from the dry box, cooled to -196°, evacuated, and sealed off by a torch. The initial ^1H nmr spectrum was taken as soon as the tubes had returned to room temperature.

The spectrum showed only a peak at 107 Hz due to the $(CH_3)_3NBHF_2$. One of the sealed nmr tubes containing a benzene solution of $(CH_3)_3NBHF_2$ was immersed in an oil bath which was maintained at 80°. A ^1H nmr spectrum, which was taken after 45 minutes of heating, showed two new peaks at 121 Hz and 111 Hz in a ratio of 2:1. Subsequent spectra showed the growth of these peaks at the expense of the starting material peak. After three hours, approximately 30% of the $(CH_3)_3NBHF_2$ had reacted and after five hours, about 50% had reacted. The nmr spectrum after 24 hours showed that approximately 80% of the $(CH_3)_3NBHF_2$ had disproportionated to the symmetrical trimethylamine-boranes, $(CH_3)_3NBF_3$ and $(CH_3)_3NBH_3$.

The second and third tubes remained at room temperature after the initial nmr spectrum of each was taken. A ^1H nmr spectrum of each of these solutions was taken at two-day intervals. After eight days, the spectra of both the benzene solution and CH_2Cl_2 solution appeared unchanged from the initial spectra.

Thermal stability of trimethylamine-fluoroborane.-- A glass apparatus as previously described was constructed and dried overnight in an oven. It was cooled to room temperature with a stream of nitrogen and charged with 0.3941 g, 4.344 mmol of $(CH_3)_3NBH_2F$. The apparatus was then cooled to -196°, evacuated, sealed off, and immersed in an oil bath. The oil bath temperature was at 110° for 16 hours and then increased to 130° for 12 hours. After cooling to room temperature, the tube was opened and a sample of the solid dissolved in benzene. The nmr spectrum of this solution

showed a peak at 125 Hz and a peak at 116 Hz in a ratio of 2:1. The peak at 125 Hz was assigned to $(CH_3)_3NBH_3$ on the basis of previous spectra for solutions of this concentration of $(CH_3)_3NBH_3$ in benzene. The broad multiplet at 116 Hz was assigned to $(CH_3)_3NBF_3$ on the basis of its chemical shift and characteristic multiplicity. As indicated by the nmr spectrum, the $(CH_3)_3NBH_2F$ had completely and cleanly disproportionated according to the following equation.

$$3\ (CH_3)_3NBH_2F \rightarrow 2\ (CH_3)_3NBH_3 + (CH_3)_3NBF_3 \qquad (3\text{-}13)$$

A sealed tube containing a small amount of freshly sublimed $(CH_3)_3NBH_2F$ was placed in an oil bath at 115°, four degrees above its melting point, for 35 minutes. The tube then was cooled to room temperature, opened, and the content was dissolved in benzene. The nmr spectrum of this solution showed only two peaks which were at 123 Hz and 112 Hz and were in a ratio of 2:1. These peaks were attributed to $(CH_3)_3NBH_3$ and $(CH_3)_3NBF_3$ respectively.

The stability of $(CH_3)_3NBH_2F$ was also investigated in benzene at reflux temperature, in benzene at room temperature, and in CH_2Cl_2 at room temperature. These experiments were done simultaneously with the similar ones investigating the thermal stability of $(CH_3)_3NBHF_2$. A sealed nmr tube containing a benzene solution of freshly sublimed $(CH_3)_3NBH_2F$ was immersed in an oil bath maintained at 80°. The nmr spectrum of this solution after 45 minutes, 90 minutes, 3 hours, and 5 hours, respectively showed no changes from the initial spectrum of a single peak at 114 Hz for $(CH_3)_3NBH_2F$. Again after 24 hours, the nmr spectrum remained

essentially unchanged.

The nmr spectra of the CH_2Cl_2 and benzene solutions contained in sealed nmr tubes which remained at room temperature showed no changes from the initial spectra after eight days.

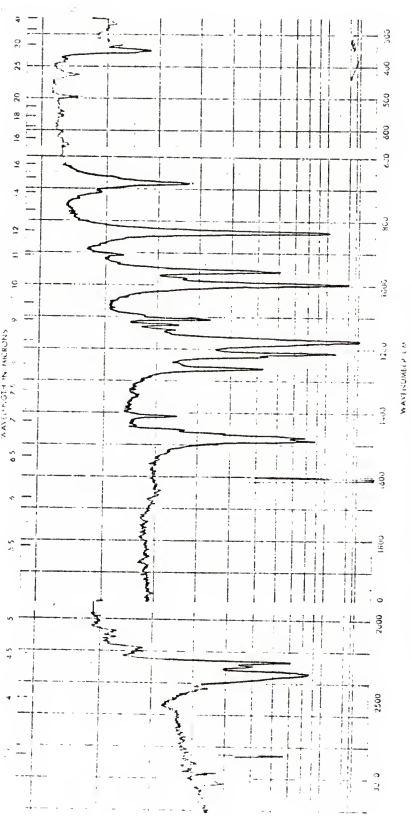

Figure 3-1. Infrared spectrum of $(CH_3)_3NBH_2F$.

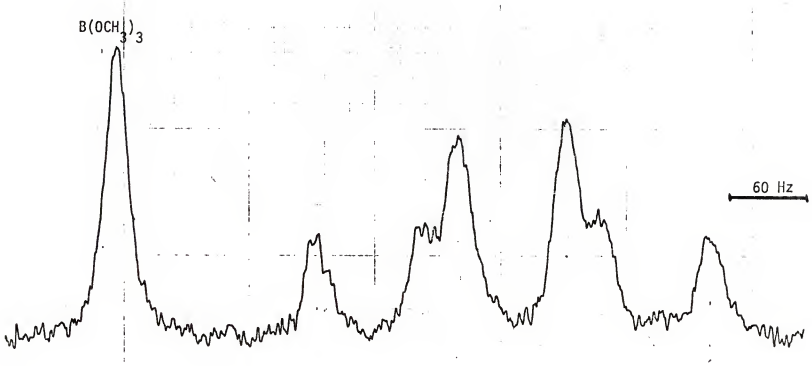

Figure 3-2. ^{11}B nmr spectrum of $(CH_3)_3NBH_2F$.

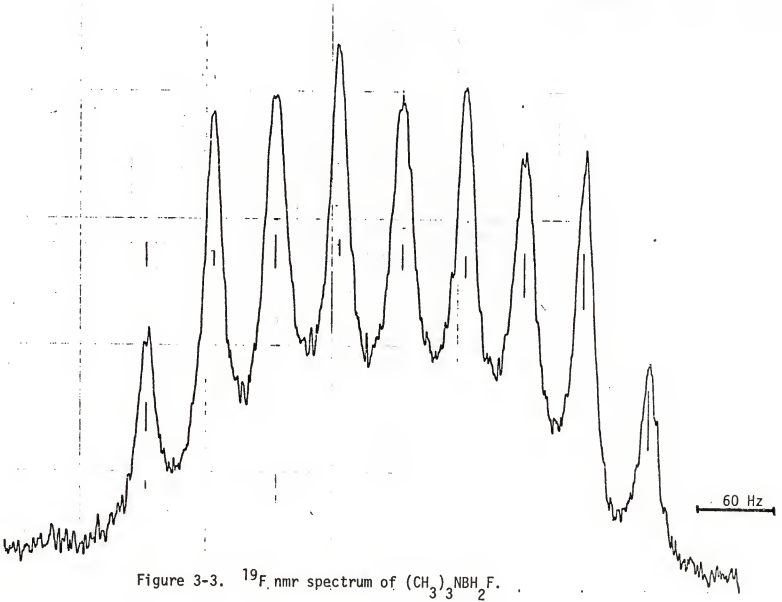

Figure 3-3. ^{19}F nmr spectrum of $(CH_3)_3NBH_2F$.

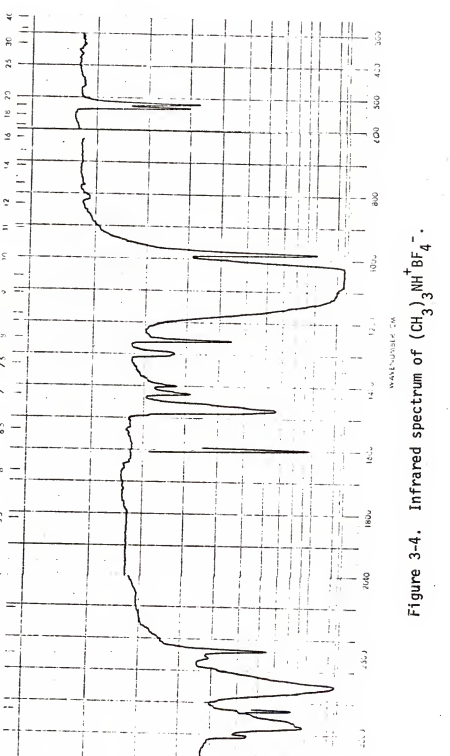

Figure 3-4. Infrared spectrum of $(CH_3)_3NH^+BF_4^-$.

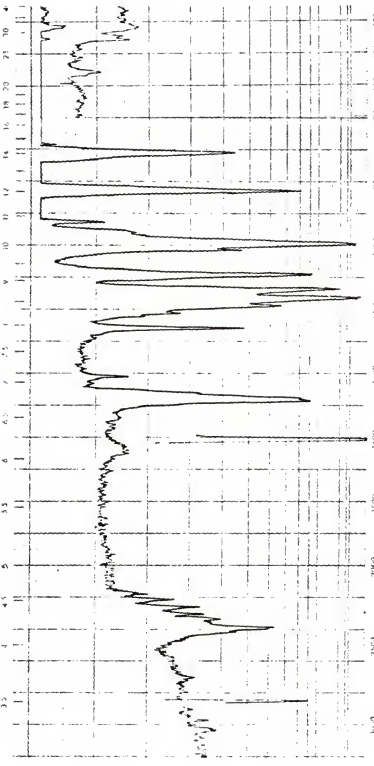

Figure 3-5. Infrared spectrum of $(CH_3)_3NBHF_2$.

Figure 3-6. ^{11}B nmr spectrum of $(CH_3)_3NBHF_2$.

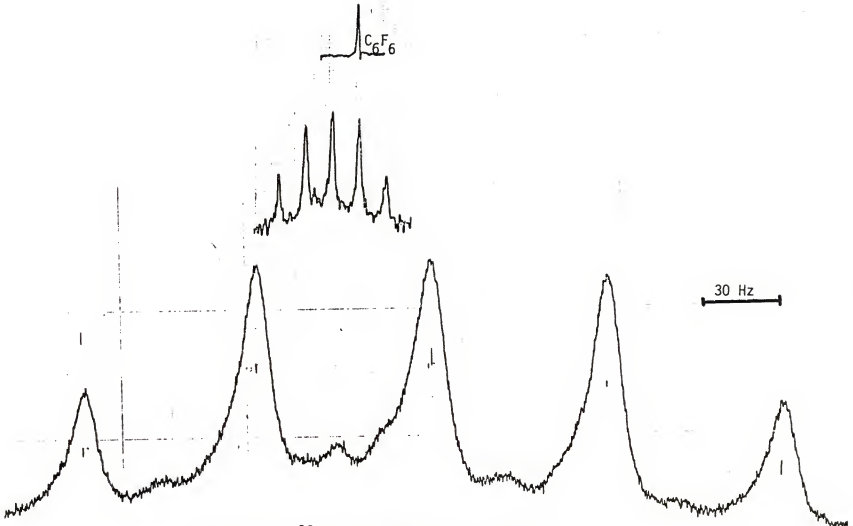

Figure 3-7. ^{19}F nmr spectrum of $(CH_3)_3NBHF_2$.

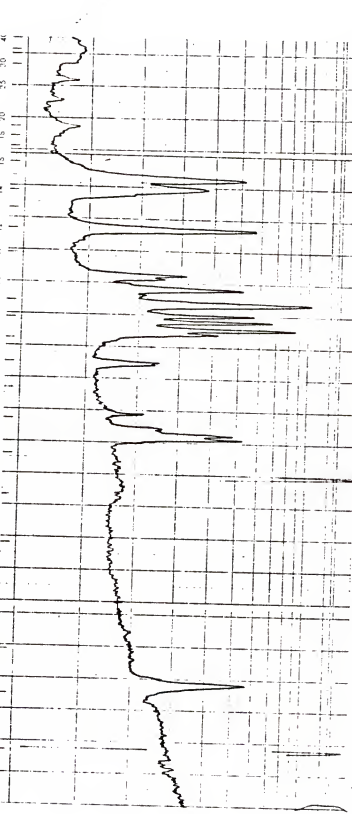

Figure 3-8. Infrared spectrum of $(CH_3)_3NBHClF$.

Figure 3-9. ^{11}B nmr spectrum of $(CH_3)_3NBHClF$.

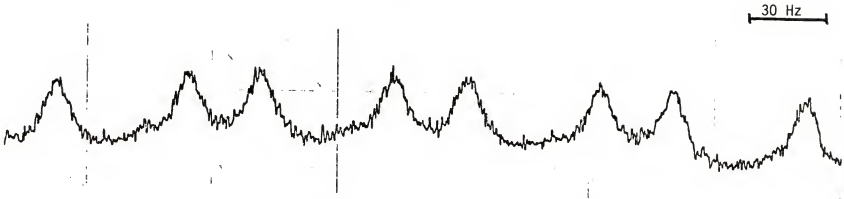

Figure 3-10. ^{19}F nmr spectrum of $(CH_3)_3NBHClF$.

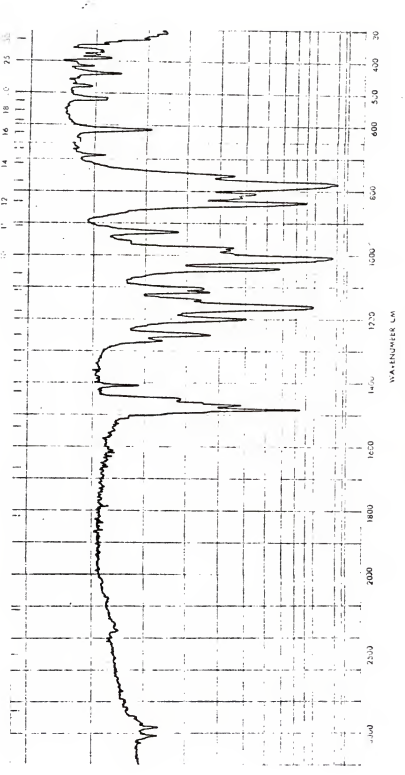

Figure 3-11. Infrared spectrum of $(CH_3)_3NBClF_2$.

Figure 3-12. ^{11}B nmr spectrum of $(CH_3)_3NBClF_2$.

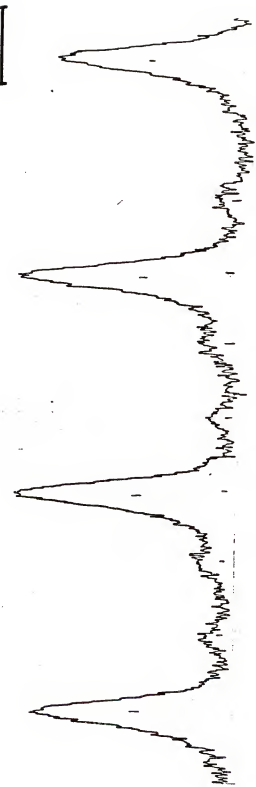

Figure 3-13. ^{19}F nmr spectrum of $(CH_3)_3NBClF_2$.

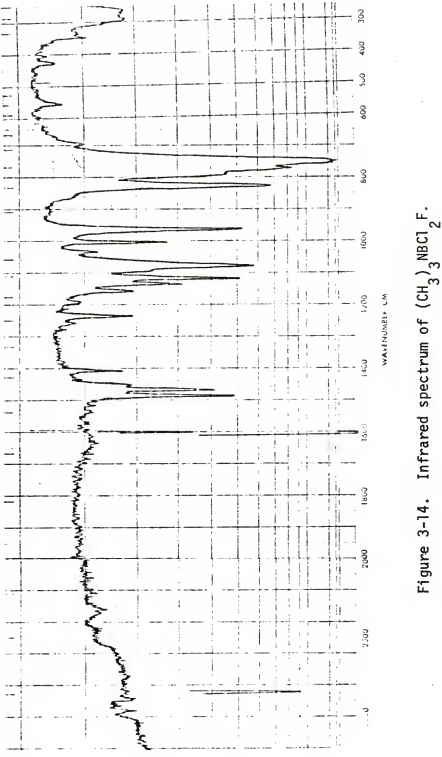

Figure 3-14. Infrared spectrum of $(CH_3)_3NBCl_2F$.

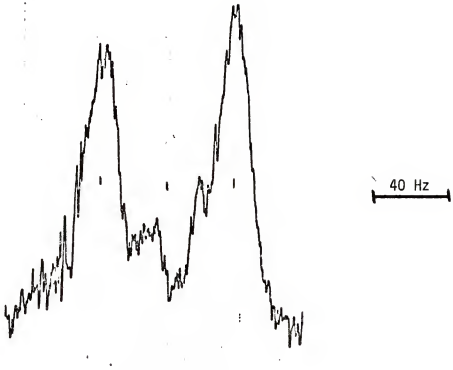

Figure 3-15. ^{11}B nmr spectrum of $(CH_3)_3NBCl_2F$.

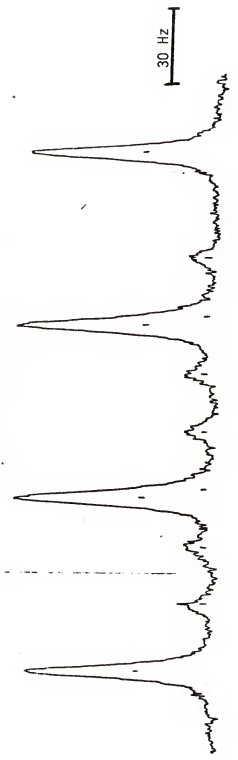

Figure 3-16. ^{19}F nmr spectrum of $(CH_3)_3NBCl_2F$.

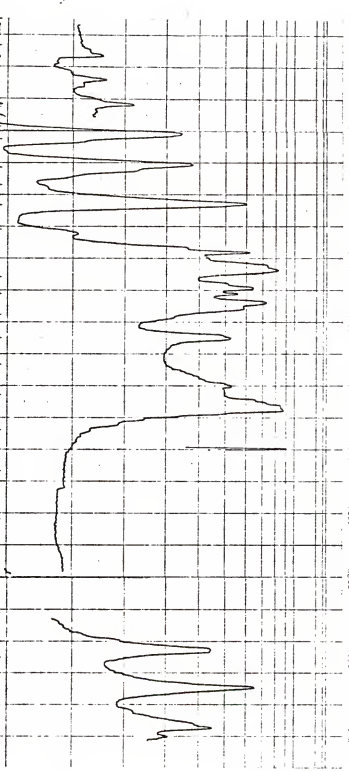

Figure 3-17. Infrared spectrum of $(CH_3)_3NBHBrF$.

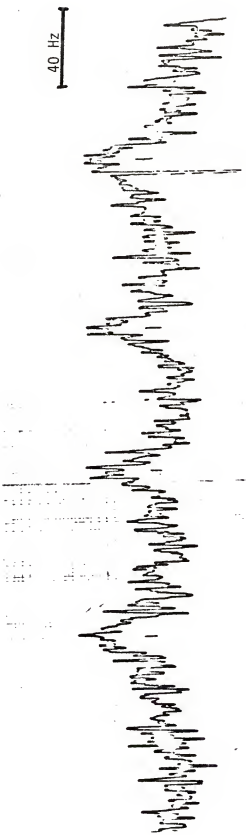

Figure 3-18. ^{11}B nmr spectrum of $(CH_3)_3NBHBrF$.

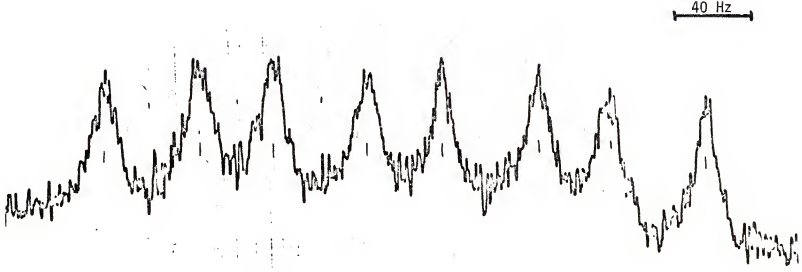

Figure 3-19. ^{19}F nmr spectrum of $(CH_3)_3NBHBrF$.

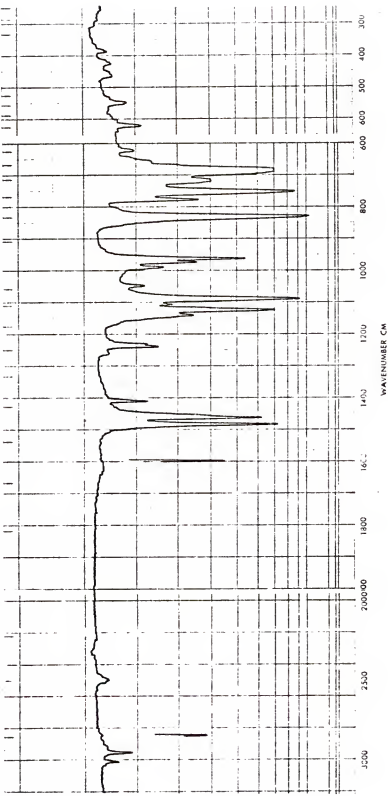

Figure 3-20. Infrared spectrum of $(CH_3)_3NBBr_2F$.

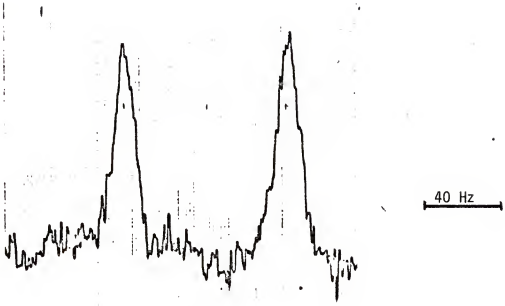

Figure 3-21. ^{11}B nmr spectrum of $(CH_3)_3NBBr_2F$.

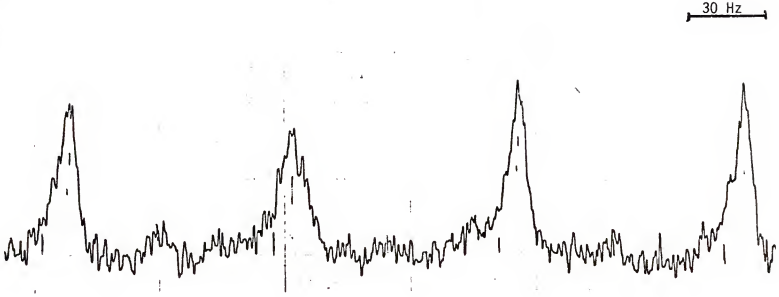

Figure 3-22. ^{19}F nmr spectrum of $(CH_3)_3NBBr_2F$.

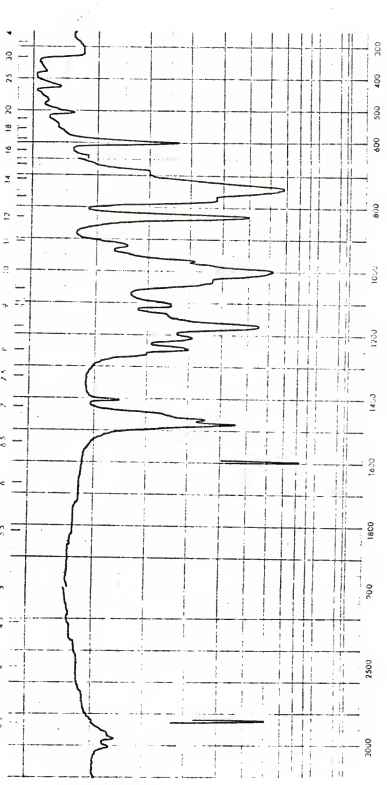

Figure 3-23. Infrared spectrum of $(CH_3)_3NBBrF_2$.

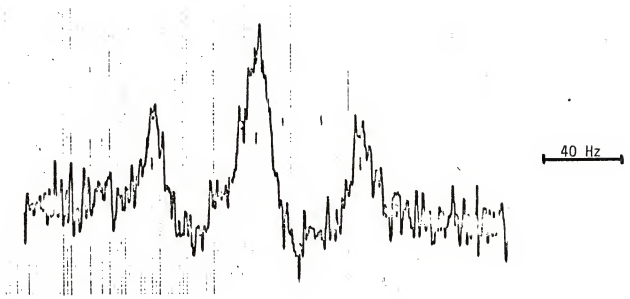

Figure 3-24. ^{11}B nmr spectrum of $(CH_3)_3NBBrF_2$.

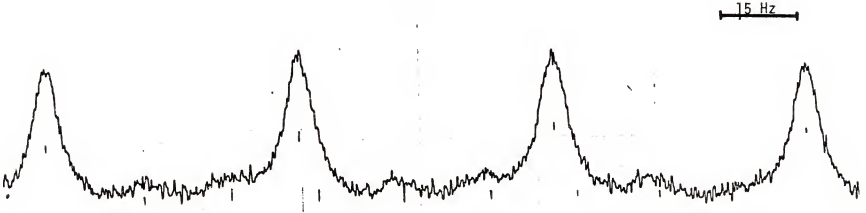

Figure 3-25. ^{19}F nmr spectrum of $(CH_3)_3NBBrF_2$.

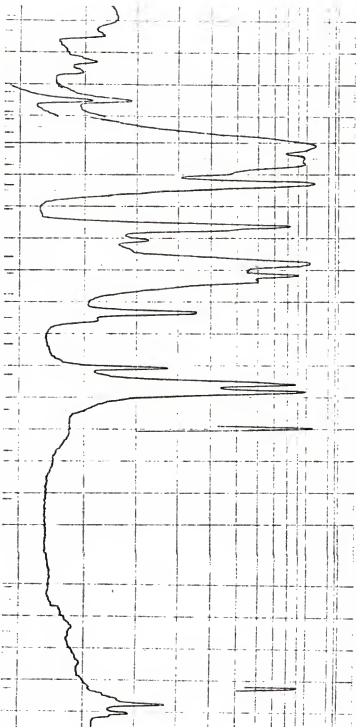

Figure 3-26. Infrared spectrum of $(CH_3)_3NBBrClF$.

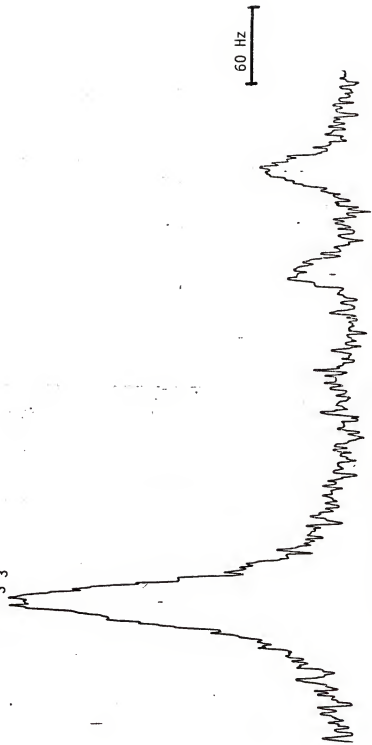

Figure 3-27. ^{11}B nmr spectrum of $(CH_3)_3NBBrClF$.

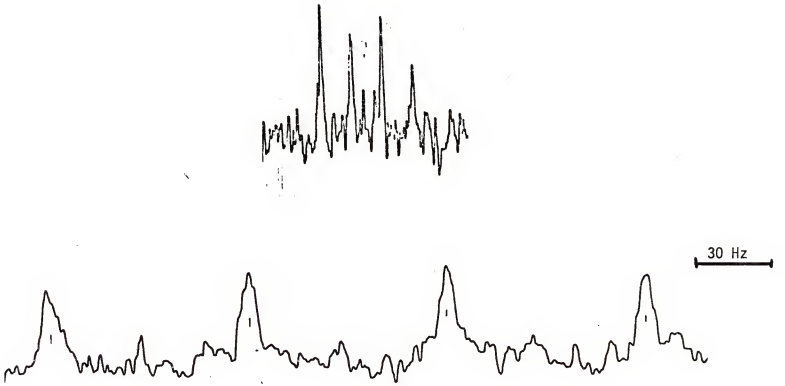

Figure 3-28. ^{19}F nmr spectrum of $(CH_3)_3NBBrClF$.

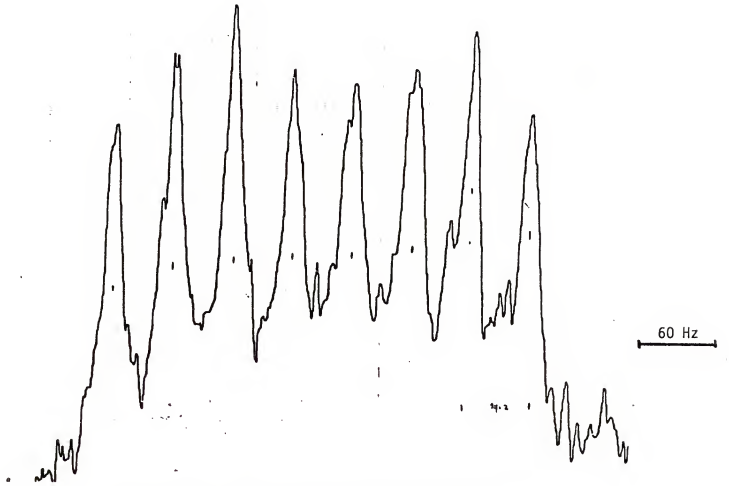

Figure 3-29. ^{19}F nmr spectrum of $(CH_3)_3NBHIF$.

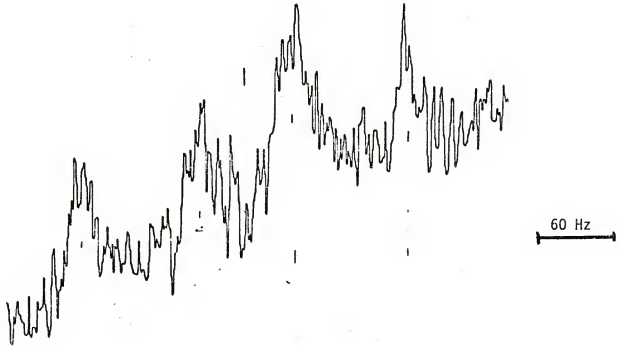

Figure 3-30. ^{11}B nmr spectrum of $(CH_3)_3NBHIF$.

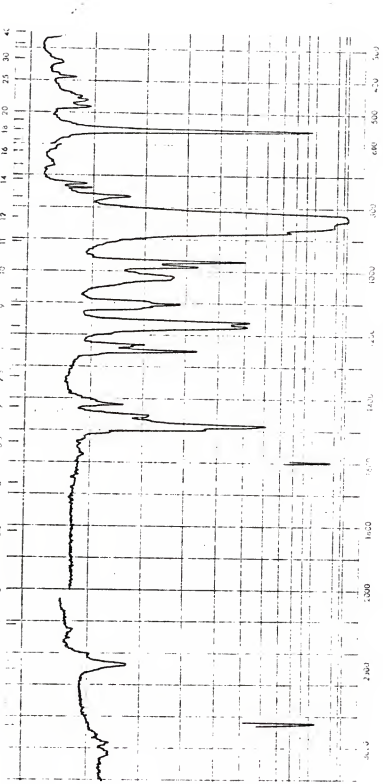

Figure 3-31. Infrared spectrum of $((CH_3)_3N)_2BHF^+PF_6^-$.

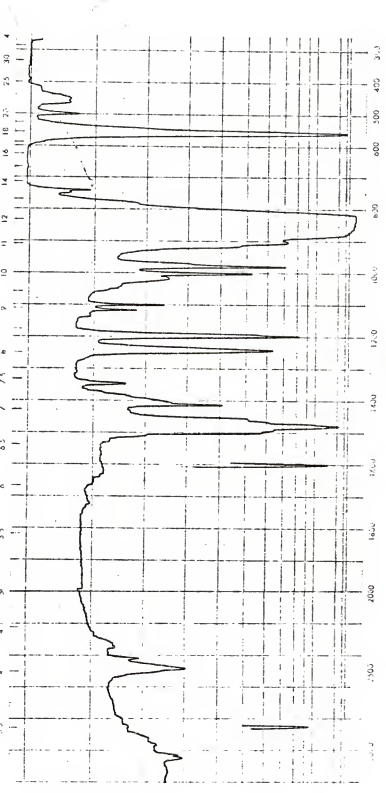

Figure 3-32. Infrared spectrum of $((CH_3)_3N)_2BH_2^+PF_6^-$.

Table 3-1

Infrared Data for Fluorosubstituted Trimethylamine-boranes[a]

$(CH_3)_3NBH_2F$:	3020(m), 2960(m), 2380-2340(s,br), 2290(m), 2270(s), 1485(s), 1470(m), 1460(m), 1450(m), 1410(w), 1260(m), 1230(m), 1220(s), 1170(s), 1105(m), 995(s), 980(w), 955(m,s), 830(s), 675(m), 490(w), 420(w), 345(m).
$(CH_3)_3NBHF_2$:	3030(w), 2410(sh), 2400(s), 2340(m), 1485(s), 1475(sh), 1460(sh), 1410(w), 1260(m), 1210(m), 1185(s), 1160(s), 1140(s), 1090(s), 1010(m), 990(s), 960(sh), 930(w-m) 825(s), 735(sh), 705(s), 455(m), 360(m).
$(CH_3)_3NBHClF$:	3030(w), 2985(w), 2440(s), 1485(s,m), 1470(m), 1450(w), 1410(w), 1260(w), 1250(w), 1155(m), 1140(s), 1115(m), 1100(m), 1060(s), 1020(m), 985(w), 975(m), 830(s), 705(m), 678(s), 530(w), 450(w), 380(w).
$(CH_3)_3NBClF_2$:	3020(w), 2960(w), 1485(s), 1470(m), 1460(sh), 1410(w), 1260(w), 1250(m), 1200(m), 1160(s), 1140(m), 1115(m), 1105(m), 1045(s), 1010(s), 985(m), 975(m), 930(m), 840(s), 820(m), 780(s), 750(m), 690(w), 610(m), 520(m), 440(m).

Table 3-1 (continued)

$(CH_3)_3NBCl_2F$: 3020(w), 2960(w), 1485(s), 1465(m), 1450(m), 1410(w), 1240(m), 1140(m), 1125(s), 1100(sh), 1085(s), 970(s), 835(s), 800(s), 780(s), 565(w), 440(w), 360(w).

$(CH_3)_3NBHBrF$: 3020(w), 2960(m), 2450(s), 1480(s), 1460(sh), 1410(w), 1250(m), 1160(m), 1140(m), 1110(m), 1095(m), 1040(s), 1020(m), 985(m), 970(sh), 835(s), 730(sh), 710(m), 640(sh), 610(m), 520(m), 440(m).

$(CH_3)_3NBBr_2F$: 3020(w), 2960(w), 1485(s), 1465(s), 1410(w), 1240(w), 1230(w), 1140(m), 1125(s), 1105(w), 1090(s), 1050(w), 990(w), 975(m), 960(m), 830(s), 780(m), 755(s), 715(m), 685(s), 620(w), 550(w), 460(w), 430(w).

$(CH_3)_3NBBrF_2$: 3020(w), 2960(w), 1485(s), 1470(m), 1410(w), 1265(sh), 1250(m), 1215(m), 1175(s), 1115(m), 1035(m), 1000(s), 970(m), 920(w), 830(s), 780(sh), 745(s), 680(sh), 600(s), 505(w).

$(CH_3)_3NBClBrF$: 3020(w), 2960(m), 1485(s), 1460(s), 1410(m), 1240(m), 1140(m), 1120(s), 1085(s), 1010(w), 975(sh), 970(s), 833(s), 795(sh), 770(s), 750(s), 730(sh), 710(s), 550(m), 465(w), 430(w).

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[a] All values are in cm^{-1}. Symbols: s = strong, m = medium, w = weak sh = shoulder, br = broad.

Table 3-2

Summary of Competitive Reactions of Hydrogen Halides with Trimethylamine-borane

mmol HX	mmol HX'	mmol $(CH_3)_3NBH_3$	Volume(ml) CH_2Cl_2 sol'n	Principal Product
2.0 HF	1.7 HBr	2.2	20	$(CH_3)_3NBH_2Br$
4.0 HF	3.4 HBr	2.2	35	$(CH_3)_3NBH_2Br$
10.0 HF	2.0 HBr	2.0	52	Equal amount $(CH_3)_3NBH_2Br$ $(CH_3)_3NBH_2F$
1.9 HF	1.9 HCl	3.8	40	$(CH_3)_3NBH_2F$
4.0 HF	4.0 HI	4.1	45	$(CH_3)_3NBH_2I$
2.4 HBr	2.5 HI	2.5	33	$(CH_3)_3NBH_2I$
0.0286 HBr	0.0286 HCl	0.0286	2.0	$(CH_3)_3NBH_2Br$

Note: Last line of table taken from Mathur[4].

CHAPTER 4

DISCUSSION

Highly successful and convenient methods have been developed for the synthesis of the Lewis acid-base adducts, $(CH_3)_3NBH_{3-n}X_n$ where X = F and n = 1 or 2, $(CH_3)_3NBHYX$ where X = F and Y = Cl or Br (the adduct where Y = I has been observed but not isolated), and $(CH_3)_3NBBrClF$. The syntheses of these adducts have been shown to occur by the following equations as previously given in Chapter 3.

$$(CH_3)_3NBH_3 + HF \rightarrow (CH_3)_3NBH_2F + H_2 \quad (3\text{-}1)$$

$$(CH_3)_3NBH_2F + HF \rightarrow (CH_3)_3NBHF_2 + H_2 \quad (3\text{-}2)$$

$$(CH_3)_3NBH_2F + HCl \rightarrow (CH_3)_3NBHClF + H_2 \quad (3\text{-}4)$$

$$(CH_3)_3NBHF_2 + Cl_2 \rightarrow (CH_3)_3NBClF_2 + HCl \quad (3\text{-}5)$$

$$(CH_3)_3NBHClF + Cl_2 \rightarrow (CH_3)_3NBCl_2F + HCl \quad (3\text{-}6)$$

$$(CH_3)_3NBH_2F + HBr \rightarrow (CH_3)_3NBHBrF + H_2 \quad (3\text{-}7)$$

$$(CH_3)_3NBH_2F + 3/2\ Br_2 \rightarrow (CH_3)_3NBBr_2F + HBr + 1/2\ H_2 \quad (3\text{-}8)$$

$$(CH_3)_3NBHF_2 + Br_2 \rightarrow (CH_3)_3NBBrF_2 + HBr \quad (3\text{-}9)$$

$$(CH_3)_3NBHClF + Br_2 \rightarrow (CH_3)_3NBBrClF + HBr \quad (3\text{-}10)$$

The method of synthesis for $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ was the fluorination of trimethylamine-borane using anhydrous hydrogen fluoride. The mixed halogenated adducts of $(CH_3)_3NBH_3$ were prepared by the direct halogenation of the partially fluorinated species.

The reaction of anhydrous hydrogen fluoride, HF, with trimethylamine-borane, $(CH_3)_3NBH_3$, was reported by Noeth and Beyer[1] to yield only the trifluorinated derivative, $(CH_3)_3NBF_3$. However, this work has found the reaction of HF and $(CH_3)_3NBH_3$ to successively produce the monofluoro, difluoro, and trifluoro derivatives, i.e., $(CH_3)_3NBH_2F$, $(CH_3)_3NBHF_2$, and $(CH_3)_3NBF_3$. The several fluorination steps were all found to be extremely fast at room temperature so that any excess over the stoichiometric amount of HF necessary to achieve the desired extent of substitution was found to produce immediate further fluorination, and eventually, $(CH_3)_3NBF_3$. The partially fluorinated products of the reaction, $(CH_3)_3NBH_2F$, and $(CH_3)_3NBHF_2$, had therefore been missed in the earlier investigation of this reaction. Also, when the reaction was done by Noeth and Beyer, there was no readily available means to observe the intermediary existence of $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ in the reaction solution. The development of nuclear magnetic resonance as an analytical tool has since provided a convenient means for observing the successive products of this reaction by their chemical shift resulting from the resonance of the methyl group.

As previously described, the reaction of HF and $(CH_3)_3NBH_3$ was rapid. Gas evolution was immediate on contact of HF with a solution of $(CH_3)_3NBH_3$. If the solution was not analyzed until gas evolution had ceased, $(CH_3)_3NBF_3$ was the only borane adduct identified. Proton nmr spectra, however, were taken during the course of the reaction on removed samples of the solution. These

spectra showed peaks due to methyl resonances other than for the starting material, $(CH_3)_3NBH_3$, or for the final product of the reaction, $(CH_3)_3NBF_3$.

It is of interest to note that in this work the new compounds, $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ were not first observed in the reaction used to develop their synthesis, i.e., the reaction of HF and $(CH_3)_3NBH_3$. Instead, their existence was suggested by the unexpected results of a reaction done to prepare an ether containing boronium species.

$$(C_2H_5)_3O^+BF_4^- + (CH_3)_3NBH_3 \rightarrow C_2H_6 + (CH_3)_3N\overset{H}{\underset{H}{B}}O(C_2H_5)_2^+BF_4^- \quad (3\text{-}3)$$

The reaction indicated by equation 3-3 was chosen as a possible synthetic route to an ether containing boronium species. Triethyloxoniumtetrafluoroborate, $(C_2H_5)_3O^+BF_4^-$, was expected to react with $(CH_3)_3NBH_3$ by means of a hydride abstraction producing ethane, C_2H_6 and leaving the boronium species, $(CH_3)_3NBH_2^+$ to which ether could coordinate. The resulting cationic species was expected to be isolated as the tetrafluoroborate salt. The reaction which occurred was not as expected but was of interest with respect to product assignment and mechanism.

As described previously, the reaction of $(C_2H_5)_3O^+BF_4^-$ with $(CH_3)_3NBH_3$ was immediate but other than ethane gave unexpected products. The new ethyl resonance in the spectrum was attributed to boron trifluoride etherate, $(C_2H_5)_2O{\cdot}BF_3$, on the basis of its chemical shift and comparison to the spectrum of an authentic sample. The three other new peaks in the spectrum were near the

methyl resonance of the starting material, $(CH_3)_3NBH_3$, at 157 Hz. Two of these peaks were slightly upfield at 152 Hz and 148 Hz and one was co-incident with the starting material peak. The peak at 152 Hz was the first of these new peaks to appear in the spectrum. To account for the initial nmr spectrum of the reaction mixture, it was entirely reasonable to postulate a reaction where the expected intermediate trigonal cationic species abstracted fluoide ion from BF_4^- instead of coordinating to ether, $(C_2H_5)_2O$. Ether would then combine with the BF_3 thus produced. The overall result would then be expressed by the following net equation.

$$(CH_3)_3NBH_3 + (C_2H_5)_3O^+BF_4^- \rightarrow (CH_3)_3NBH_2F + C_2H_6 + (C_2H_5)_2O{\cdot}BF_3 \quad (4\text{-}1)$$

The reaction was done with $(CH_3)_3NBH_3$ in slight excess of a 1:1 molar ratio of reactants. The hydride abstraction to produce C_2H_6 was fast so that the ethyl peaks of the starting material had almost completely disappeared in the first nmr spectrum which was taken shortly after the mixing of the reactants. This was accompanied by the formation of the peak at 152 Hz. After a few minutes of reaction, an nmr spectrum showed the appearance of the peak at 148 Hz and that the peak at 152 Hz had diminished in intensity.

The new peak at 148 Hz could have developed from the further reaction of the oxonium salt with the product of the initial reaction according to the following equation.

$$(CH_3)_3NBH_2F + (C_2H_5)_3O^+BF_4^- \rightarrow (CH_3)_3NBHF_2 + C_2H_6 + (C_2H_5)_2O{\cdot}BF_3 \quad (4\text{-}2)$$

However, the quartet and triplet resulting from the ethyl resonance of the starting material had almost completely disappeared from the first spectrum of the reaction mixture. Gas evolution had ceased shortly after mixing the reactants. This also indicated that the oxonium salt had been used and was not available for further reaction. The peak at 148 Hz was, therefore, postulated to be the result of an interaction of the products of the initial reaction. This consideration was based on the fact that boron trifluoride etherate is known to exist in rapid equilibrium as given in equation 4-3.[18] As a result of this equilibrium, free BF_3 was available in the reaction mixture so that further fluorination could occur as given by equation 4-4.

$$(C_2H_5)_2O{\cdot}BF_3 \rightleftharpoons (C_2H_5)_2O + BF_3 \qquad (4\text{-}3)$$

$$(C_2H_5)_2O + BF_3 + (CH_3)_3NBH_2F \rightarrow (CH_3)_3NBHF_2 + (C_2H_5)_2O{\cdot}BF_2H \qquad (4\text{-}4)$$

The development of the peak at 157 Hz was indicative of a new species with the same chemical shift as $(CH_3)_3NBH_3$. The chemical shift of $(CH_3)_3NBF_3$ is known to be the same as for the starting material of the reaction, $(CH_3)_3NBH_3$ in CH_2Cl_2. Even though the peak for $(CH_3)_3NBF_3$ has a characteristic multiplicity, a small amount of unreacted $(CH_3)_3NBH_3$ would result in a symmetrical peak as was observed in the spectrum. Its formation was accounted for by further fluorination of $(CH_3)_3NBHF_2$ by the free Lewis acid, BF_2H, which resulted from the equilibrium established by the etherate formed in equation 4-4. Therefore, equations 4-5 and 4-6 were used to account for the final product

of the reaction, $(CH_3)_3NBF_3$.

$$(C_2H_5)_2O{\cdot}BF_2H \rightleftharpoons (C_2H_5)_2O + BF_2H \quad (4\text{-}5)$$

$$(C_2H_5)_2O + BF_2H + (CH_3)_3NBHF_2 \rightarrow (CH_3)_3NBF_3 + (C_2H_5)_2O{\cdot}BFH_2 \quad (4\text{-}6)$$

The observation that the peaks attributed to the ethyl resonance of $(C_2H_5)_2O{\cdot}BF_3$ in the initial spectrum shifted slightly upfield in subsequent spectra of the reaction mixture was accounted for by the sequential formation of the ether adducts, $(C_2H_5)_2O{\cdot}BF_2H$ and $(C_2H_5)_2O{\cdot}BFH_2$. Additional support was given to the mechanism of the reaction as represented by equations 4-3 to 4-6 by the fact that the progress of the reaction was influenced by a shift in the etherate equilibrium (equation 4-3). If the reaction was carried out with half of the solvent replaced by ether, the reaction, as indicated by the peak evolvement in the nmr spectra, was slowed considerably. This was in accord with the expectation that the etherate equilibrium would be shifted towards the etherate making BF_3 less available for reaction. When a nearly 1:1 mixture of $(C_2H_5)_3O^+BF_4^-$ and $(CH_3)_3NBH_3$ was stirred with NaF, the reaction did not progress beyond the formation of the peak at 152 Hz. In this case, the fluoride ion was effective in eliminating the reactivity of BF_3 by complexing it as BF_4^-. In contrast to the ether complex of BF_3, salts of the fluoride complex do not react with borane adducts.

Support for the assignment of the new peaks at 152 Hz and 148 Hz as $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ was gained from the reaction of chlorine with the reaction mixture of $(CH_3)_3NBH_3$ and $(C_2H_5)_3O^+BF_4^-$.

The chemical shifts of the three quartets which resulted in the nmr spectrum upon chlorination were identical to those reported by Hartman and Miller[5] for mixtures of chlorofluoroborane adducts, and later observed in this work for $(CH_3)_3NBCl_2F$, $(CH_3)_3NBClF_2$, and $(CH_3)_3NBCl_3$. These chloro derivatives could only have resulted if $(CH_3)_3NBH_2F$, $(CH_3)_3NBHF_2$, and $(CH_3)_3NBH_3$ had been present in the mixture respectively.

It appeared impossible to separate and identify $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ as products in the reaction of $(C_2H_5)_3O^+BF_4^-$ and $(CH_3)_3NBH_3$. Therefore, a method to prepare these compounds individually was investigated, in particular, the fluorination of $(CH_3)_3NBH_3$ using anhydrous HF. It was curious that this reaction which involved the weakest acid of the hydrogen halides would produce, as reported in the literature[1], the trihalogenated species so readily when the other hydrogen halides, HCl, HBr, and HI, were known to only monohalogenate $(CH_3)_3NBH_3$ at room temperature. The reaction was, therefore, done with careful observation of the nmr spectra of the solution in order to observe the methyl resonance for a partially fluorinated species.

Nmr spectra taken at intervals of the CH_2Cl_2 solution through which HF was passed showed a continual and successive evolvement of peaks due to a methyl resonance. As the initial peak at 157 Hz disappeared, a peak at 152 Hz appeared and increased. As soon as the peak at 157 Hz was lost from the spectrum, a peak at 148 Hz appeared and increased at the expense of the

peak at 152 Hz. When the peak at 152 Hz had disappeared from the spectrum, a peak appeared at 157 Hz which displayed the multiplicity characteristic of $(CH_3)_3NBF_3$. The peak at 157 Hz increased until the peak at 148 Hz had disappeared and then it remained unchanged in the spectrum. The fluorination reaction was extremely fast and seemed to be limited only by the rate of flow of HF. The reaction required repetition until a "feel" for its progress as observed in the careful analysis of the nmr spectra of the reaction solution enabled the worker to prepare $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ individually with the ammonium salt, $(CH_3)_3NH^+BF_4^-$, as the only other product of the reaction.

The trimethylamine-fluoroboranes are of fairly high volatility so that their separation from the ammonium salt was easily accomplished by sublimation. They sublimed quickly in vacuo at room temperature onto a dry ice/acetone cold finger. Their volatilities, however, are so similar that a mixture of them can not be separated completely by fractional sublimation even at 0^o. These white crystalline solids are also very similar in their solubility in common laboratory solvents and are therefore not easily separable on the basis of solubility differences.

It was found that the monofluoro and difluoro derivatives of trimethylamine-borane could only be conveniently prepared as pure compounds if the product of each step was isolated in the successive fluorination of $(CH_3)_3NBH_3$ using anhydrous HF. The success of the reaction as indicated by yields of 70 - 85%

of pure desired product was worth the careful monitoring of the reaction by means of nmr spectra so that any excess of the stoichiometric amount of HF for the desired extent of fluorination was avoided.

It should be noted that the reactivity of $(CH_3)_3NBH_3$ appeared to decrease on successive fluorination but not as markedly as for chlorination, bromination or iodination for which dihalogenation is not possible at room temperature. Halogenation of $(CH_3)_3NBH_3$ is considered to decrease the hydridic character of the remaining B-H bonds such that further halogenation by the hydrogen halide is not possible. The reactivity difference of the trimethylamine-fluoroboranes is, however, large enough so that the reaction of HF and $(CH_3)_3NBH_3$ proceded in a cleanly stepwise fashion. However, further fluorination is very difficult to avoid, especially in the preparation of $(CH_3)_3NBH_2F$. It was easier to avoid in the preparation of $(CH_3)_3NBHF_2$ since there appeared in the nmr spectrum a more definite break in the peak evolvement from 148 Hz to 157 Hz. The final step in the fluorination process also took somewhat longer as compared to the steps for $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ which took approximately the same length of time provided that the flow of HF was constant throughout the whole sequence of fluorination.

The synthesis of $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ was also achieved using a CH_2Cl_2 solution of HF but this was found much less convenient than using anhydrous HF. This method worked reasonably

well for the preparation of $(CH_3)_3NBH_2F$ but for $(CH_3)_3NBHF_2$ and $(CH_3)_3NBF_3$ it required the addition of HF solution in excess of the stoichiometry in order to achieve the desired extent of fluorination. The addition of HF to the reaction by means of solution was more difficult to control than addition of HF by rate of flow, as the concentration of an HF solution decreased quickly on standing.

One other method for the synthesis of $(CH_3)_3NBH_2F$ was explored. It involved an exchange of halide between $(CH_3)_3NBH_2I$ and $((C_6H_5)_3P)_2NF$ to give the desired $(CH_3)_3NBH_2F$. This method would have advantages if the $((C_6H_5)_3P)_2NCl$ could be more easily and purely converted to $((C_6H_5)_3P)_2NF$. Small amounts of unconverted chloride salt were found to cause eventual contamination of the product with $(CH_3)_3NBH_2Cl$. Therefore, the synthesis of $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ is best achieved by the stepwise fluorination of $(CH_3)_3NBH_3$ using anhydrous gaseous HF.

The omnipresent other reaction in the fluorination of $(CH_3)_3NBH_3$ by HF was the formation of trimethylammonium tetrafluoroborate. This reaction prevented the quantitative yield of partially fluorinated amine-borane, but it did not interfere with their isolation. The desired products were easily separated from the ammonium salt in the sublimation process since the salt did not sublime. The ammonium salt was formed in higher yield if the fluorination process was continued for a longer time.

The partially fluorinated trimethylamine-boranes were found

to differ in their stability towards ammonium salt formation on exposure to moisture. Freshly sublimed $(CH_3)_3NBH_2F$ could be handled in the laboratory atmosphere prior to its use in a reaction with negligible amount of ammonium salt formation. It could be stored in a screwcap glass vial on the shelf for a period of a week before resublimation was necessary prior to its use. Even after long standing on the shelf, the solid was found to be 90 - 95% $(CH_3)_3NBH_2F$ when sublimed. By contrast, freshly sublimed $(CH_3)_3NBHF_2$ was found to form ammonium salt immediately on contact with atmospheric moisture and therefore had to be handled in a dry box. The easiest method found to handle the $(CH_3)_3NBHF_2$ was to place the solid from the reaction mixture which contained it and the ammonium salt in a flask which was then evacuated and stored in a desiccator. When $(CH_3)_3NBHF_2$ was needed for a reaction, an amount of this solid was transferred to a small sublimator in a dry box. After sublimation, the sublimator was returned to a dry box and the $(CH_3)_3NBHF_2$ collected so that its handling was completely in inert conditions. After shelf storage of $(CH_3)_3NBHF_2$ in a screwcapped glass vial for a few months, the solid was found to be only 40% $(CH_3)_3NBHF_2$ when sublimed. However, either CH_2Cl_2 or benzene solutions of both $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ which were prepared free of moisture and sealed in nmr tubes remained unchanged after long standing at room temperature as indicated by their nmr spectra.

The thermal stability of both $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$

was also investigated. Both of these partially fluorinated trimethylamine-boranes were found to be unstable with respect to disproportionation at temperatures slightly above their respective melting points. At these conditions, disproportionation was found to be complete and fast. The process was shown to occur according to equations 3-12 and 3-13.

$$3\ (CH_3)_3NBHF_2 \rightarrow (CH_3)_3NBH_3 + 2\ (CH_3)_3NBF_3 \qquad (3\text{-}12)$$

$$3\ (CH_3)_3NBH_2F \rightarrow 2\ (CH_3)_3NBH_3 + (CH_3)_3NBF_3 \qquad (3\text{-}13)$$

At conditions less severe, $(CH_3)_3NBH_2F$ was much more stable than $(CH_3)_3NBHF_2$ towards disproportionation. A benzene solution of $(CH_3)_3NBH_2F$ in a sealed nmr tube and at the temperature of reflux remained unchanged as indicated by ^1H nmr spectra. However, ^1H nmr spectra of a benzene solution of $(CH_3)_3NBHF_2$ at the same conditions showed that approximately 80% of the $(CH_3)_3NBHF_2$ had disproportionated to form the symmetrical boranes, $(CH_3)_3NBF_3$ and $(CH_3)_3NBH_3$, in a 2:1 ratio.

It has been suggested that the disproportionation of the partially chlorosubstituted trimethylamine-boranes involves the following sequences: the dissociation of the B-N bond, the subsequent disproportionation of the free borane and finally a recombination of the products of the disproportionation with $(CH_3)_3N$[19]. The presence of free trimethylamine in the reaction mixture could then be detected by utilizing it in a known reaction, such as with an amine-iodoborane to form a cationic species. In order to ascertain whether the disproportionation of the

partially fluorosubstituted trimethylamine-boranes involved a dissociative step, solutions of them and 4-picoline-iodoborane, $C_6H_7NBH_2I$, were prepared in an nmr tube which was then sealed. 4-picoline-iodoborane was chosen as trapping agent for the $(CH_3)_3N$ since its methyl resonance provides a convenient means to study the reaction by ^1H nmr and it is known to readily form a cationic species, $C_6H_7N(CH_3)_3NBH_2^+$, with $(CH_3)_3N$.[20] Benzene was chosen as the solvent so that the iodide salt of the cation would be precipitated from solution.

Trimethylamine-fluoroborane, $(CH_3)_3NBH_2F$ (0.0273 g, 0.300 mmol), was placed in a nmr tube fitted with an 18/7 socket joint and taken into a dry box. In the dry box, 0.5 ml of dry benzene was added to dissolve the $(CH_3)_3NBH_2F$. To this solution, 0.5 ml of a benzene solution of freshly made 4-picoline-iodoborane was added to provide 0.5 mmol of $C_6H_7NBH_2I$. The nmr tube was then removed from the dry box, cooled to -78°, evacuated, and sealed off using a torch. Since disproportionation of $(CH_3)_3NBH_2F$ was not observed at room temperature, the nmr spectrum of this solution was expected to be that for the reactants. The nmr spectrum of the reaction solution after 1 hour, however, showed two new peaks in addition to the starting material peaks at 98 Hz for $C_6H_7NBH_2I$ and 114 Hz for $(CH_3)_3NBH_2F$. The larger new peak was at 128 Hz, which on the basis of previous spectra is the chemical shift for $(CH_3)_3NBH_2I$ in benzene. The other peak of lesser intensity was at 102 Hz. Trimethylamine was

passed through the solution after it had remained at room temperature overnight. A white solid was precipitated from the solution. The nmr spectrum of the solution showed that the peak at 98 Hz had been eliminated and that the peak at 128 Hz had been partially eliminated, indicating that these peaks had been due to amine-iodoboranes. A small symmetrical peak remained at 128 Hz. The peak at 102 Hz was enhanced by the addition of a small amount of 4-picoline-borane, $C_6H_7NBH_3$.

Prior to the addition of $(CH_3)_3N$, the reaction solution remained clear and colorless. The nmr spectra of the reaction mixture indicated that a considerable amount of $(CH_3)_3NBH_2I$ had formed. It appeared that on mixing $(CH_3)_3NBH_2F$ and $C_6H_7NBH_2I$, a rapid exchange of F for I occurred so that at least initially, the products of the reaction were $(CH_3)_3NBH_2I$ and $C_6H_7NBH_2F$.

Since the chemical shifts of amine-boranes are very prone to concentration shifts in benzene[21], and thereby more difficult to assign, the reaction was repeated as described above, but with CH_2Cl_2 as the solvent and a 1:1 molar ratio of reactants. The sealed nmr tube in this reaction contained 0.30 mmol of $(CH_3)_3NBH_2F$ and 0.30 mmol of $C_6H_7NBH_2I$ in 1.0 ml of CH_2Cl_2. The nmr spectrum of the solution after it had remained overnight showed the principal new peaks to be at 169 Hz and 157 Hz. After several days at room temperature, the nmr spectrum was unchanged and showed three peaks, which in order of their intensity were at 169 Hz, 157 Hz, and 150 Hz. The only peak assigned with certainty was at 169 Hz. It was shown

to be solely due to $(CH_3)_3NBH_2I$. The peak at 157 Hz had in previous spectra been shown to be due to methyl resonance of $(CH_3)_3NBH_3$ alone, or a mixture of $(CH_3)_3NBH_3$ and $(CH_3)_3NBF_3$, if it was without multiplicity as in this spectrum. The peak at 150 Hz had been observed for a CH_2Cl_2 solution of a mixture of $C_6H_7NBH_3$ and $C_6H_7NBH_2I$. Any fluorosubstituted 4-picoline-boranes were also expected to be found at this resonance. The peak at 169 Hz and the peak at 157 Hz were assigned to the methyl resonance of trimethylamine adducts and the peak at 150 Hz was assigned to the methyl resonance of 4-picoline adducts. The nmr spectrum therefore indicates this reaction to be much more complex, involving further reactions of the species involved in the initial step of the reaction. The initial step of this reaction was considered to be an exchange as shown in the following equation.

$$(CH_3)_3NBH_2F + C_6H_7NBH_2I \rightarrow (CH_3)_3NBH_2I + C_6H_7NBH_2F \qquad (4\text{-}7)$$

The ^{19}F nmr spectrum of this reaction mixture showed only two quartets. On the basis of previous, known spectra, they were assigned as $(CH_3)_3NBF_3$ and $C_6H_7NBF_3$. The ratio of $C_6H_7NBF_3$ to $(CH_3)_3NBF_3$ was 3.54:1.00 as determined by the technique of cutting out the peaks of the spectrum and weighing the paper.

A product assignment of this reaction was attempted on the basis of the combined information of the ^1H and ^{19}F nmr spectra, previously known reactions and stoichiometry. The most satisfactory accounting of the reaction was obtained based on the following set of facts (1-2) and assumptions (3-10).

1) After 5 days at room temperature, no $(CH_3)_3NBH_2F$ remains as indicated by the nmr spectrum.

2) The peak at 169 Hz is solely $(CH_3)_3NBH_2I$.

3) There is an initial, rapid exchange of F for I as in equation 4-7:

$$(CH_3)_3NBH_2F + C_6H_7NBH_2I \rightleftharpoons (CH_3)_3NBH_2I + C_6H_7NBH_2F \quad (4\text{-}7)$$

4) The only iodine containing species are unreacted $C_6H_7NBH_2I$ and $(CH_3)_3NBH_2I$.

5) The $(CH_3)_3NBH_2F$ not involved in the initial exchange is converted to $(CH_3)_3NBH_3$ and $(CH_3)_3NBF_3$ via a disproportionation mechanism that proceeds in competition with the exchange.

6) The peak at 157 Hz is assigned to $(CH_3)_3NBH_3$ and $(CH_3)_3NBF_3$.

7) The chemical shifts of the 4-picoline adducts are seen as one peak in the ^1H nmr.

8) The $C_6H_7NBH_2F$ formed in the initial exchange proceeds to $C_6H_7NBH_3$ and $C_6H_7NBF_3$ analogous to the behavior of $(CH_3)_3NBH_2F$. Hence at the end of the reaction, there is no $C_6H_7NBH_2F$.

9) Trimethylamine-borane establishes an equilibrium with $C_6H_7NBH_2I$.[22]

$$(CH_3)_3NBH_3 + C_6H_7NBH_2I \rightleftharpoons C_6H_7NBH_3 + (CH_3)_3NBH_2I \; ; \; K_{37}^{o} = 0.27$$

10) 4-picoline-borane reacts with $C_6H_7NBH_2I$ according to the following equation.[8]

$$C_6H_7NBH_3 + C_6H_7NBH_2I \rightleftharpoons C_6H_7NBH_2^+I^- + 1/2\ B_2H_6$$

Based on the initial moles of reactants, the measured peak height for $(CH_3)_3NBH_2I$ in the ^1H nmr, the relative amounts of $C_6H_7NBF_3$ and $(CH_3)_3NBF_3$ as obtained from ^{19}F nmr spectra, the K_{eq} of assumption 9, and the other assumptions, the following product analysis was obtained in mmol.

	BF_3	BH_3	BH_2I	$BH_2^+I^-$
$(CH_3)_3N$ adduct	0.022	0.120	0.158	
C_6H_7N adduct	0.078	0.0154	0.075	0.067

Even though the above is the best possible description of the reaction of $C_6H_7NBH_2I$ and $(CH_3)_3NBH_2F$, it is not entirely adequate. The peak height at 157 Hz as calculated from the above data is almost 5 divisions more than the observed peak height. Also, the K_{eq} of assumption 9 as calculated from this data is 0.72. The discrepancy which remains even on exhaustive treatment of the data can be considered either due to the fact that the system did not attain equilibrium, or yet another species is present in the mixture that does not contain fluorine.

Therefore, it is reported that the reaction of $(CH_3)_3NBH_2F$ and $C_6H_7NBH_2I$ results in $(CH_3)_3NBH_2I$, $(CH_3)_3NBH_3$, $(CH_3)_3NBF_3$, $C_6H_7NBH_2I$, $C_6H_7NBH_3$, $C_6H_7NBF_3$, and $(C_6H_7N)_2BH_2^+I^-$ on the basis of the above analysis of the ^1H and ^{19}F nmr spectra.

The reaction of $(CH_3)_3NBHF_2$ and $C_6H_7NBH_2I$ carried out in an analogous manner to that for $(CH_3)_3NBH_2F$ was briefly investigated. The ^1H nmr spectrum taken several hours after mixing showed reaction had occurred to a small extent. However, after several days at

room temperature, the nmr spectrum of this reaction was similar to that resulting from the reaction of $C_6H_7NBH_2I$ and $(CH_3)_3NBH_2F$.

Long term heating at elevated temperatures (160°) for a 1:1 mixture of $(CH_3)_3NBH_3$ and $(CH_3)_3NBF_3$ resulted only in the recovery of the starting materials. As indicated by the above experiments, in the fluorosubstituted series of trimethylamine-borane, the symmetrical trimethylamine-boranes, $(CH_3)_3NBH_3$ and $(CH_3)_3NBF_3$, rather than the partially fluorinated trimethylamine-boranes, $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$, are thermodynamically favored.

The relative stabilities of trimethylamine-fluoroborane and trimethylamine-difluoroborane with respect to disproportionation were the reverse of the analogous chloro adducts. Wiggins[19] has reported that $(CH_3)_3NBHCl_2$ was the more stable of the two partially substituted boranes. Long term heating of $(CH_3)_3NBHCl_2$ at 185° resulted in the recovery of the starting material with only a small amount of $(CH_3)_3NBCl_3$. A 1:1 mixture of $(CH_3)_3NBH_3$ and $(CH_3)_3NBCl_3$ that was heated for 9-10 hours at 150° was found to give mono- and dihalogenated amine-boranes with no evidence of the starting material. The heating of a mixture of $(CH_3)_3NBH_3$ and $(CH_3)_3NBCl_3$ in a ratio of 1:2 and 2:1 resulted solely in $(CH_3)_3BHCl_2$ and $(CH_3)_3NBH_2Cl$ respectively. Therefore, as Wiggins noted, $(CH_3)_3NBHCl_2$ has a special stability associated with it. However, the analogous fluoro adduct, $(CH_3)_3NBHF_2$, has been shown in this work to have a lesser stability than $(CH_3)_3NBH_2F$.

A similar contrast of stabilities has been found for $(C_2H_5)_3NBHCl_2$ and $(C_2H_5)_3NBHF_2$. Ratajaczak[23] has found the dichloro

species to be particularly stable whereas this and other work has found difluoro species to be particularly unstable with respect to disproportionation.

Attempts to prepare $(C_2H_5)_3NBHF_2$ in this work were unsuccessful. Analogously to the fluorination of $(CH_3)_3NBH_3$, HF was passed through a CH_2Cl_2 solution of $(C_2H_5)_3NBH_3$. There was immediate gas evolution. Proton nmr spectra of the solution showed that a new set of peaks due to ethyl hydrogens developed from the peaks of the starting material. However, in the nmr spectra, the new set of peaks quickly evolved to a doublet of quartets in the methylene region as gas evolution ceased. The doublet of quartets was found to be due to the presence of an ammonium salt. No fluorinated triethylamine-borane was isolated from the reaction. An attempt to displace $(CH_3)_3N$ by $(C_2H_5)_3N$ in a benzene solution of $(CH_3)_3NBHF_2$ at reflux temperature was also unsuccessful.

Dazord and Monegeot[24] have prepared $(C_2H_5)_3NBHF_2$ by condensing BHF_2 onto $(C_2H_5)_3N$ at -140° and have confirmed its existence at low temperature on the basis of ^1H, ^{11}B, and ^{19}F nmr spectra. They also reported that it was extremely unstable as the ^{11}B and ^{19}F nmr spectra of $(C_2H_5)_3NBHF_2$ were observed to change quickly into the spectra for $(C_2H_5)_3NBH_3$ and $(C_2H_5)_3NBF_3$ when it was warmed above the preparation temperature. Triethylamine-difluoroborane was found to decompose instantly if it was brought to room temperature.

Both this and the above work have shown that the stability of $(C_2H_5)_3NBHF_2$ is drastically different from that of $(CH_3)_3NBHF_2$.

It has seemed reasonable to attribute some of this difference to a steric factor. The increased bulk of the ethyl groups on the amine contributes to preventing its existence at ordinary conditions.

It was of interest to investigate the reactivity of the new compounds, $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ towards the other hydrogen halides, HCl, HBr, and HI, and towards the halogens, Cl_2, Br_2, and I_2. The purpose was not only to relate the chemical properties of $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ to those of other mono- and disubstituted trimethylamine-boranes, but also to utilize the reactivity towards further halogenation to create a series of trimethylamine-mixedhaloboranes in which one of the halogen substitutes was fluorine.

The consideration of the reactivity of $(CH_3)_3NBH_2F$ towards HX, where X = Cl, Br, or I, should be prefaced by a comment on the reactivity of the unsubstituted trimethylamine-borane, $(CH_3)_3NBH_3$, towards the family of hydrogen halides. The other monohalo derivatives of trimethylamine-borane, $(CH_3)_3NBH_2X$, where X = Cl, Br, or I, can be easily prepared at room temperature by the reaction of $(CH_3)_3NBH_3$ and the appropriate hydrogen halide. As described in Chapter 3, and Table 3-2, a qualitative examination of the reactivity of HX towards $(CH_3)_3NBH_3$ was made by mixing a CH_2Cl_2 solution of $(CH_3)_3NBH_3$ and a CH_2Cl_2 solution of two different hydrogen halides and observing the reaction by means of ^1H nmr. Qualitatively, the following order of reactivity of HX towards

$(CH_3)_3NBH_3$ for monohalogenation was observed.

$$HI > HBr \gg HF > HCl$$

The order of the reactivity of HX towards $(CH_3)_3NBH_3$ was irregular with respect to its explanation on the basis of any single property of HX such as acid strength, electronegativity of the halogen, or size of the halogen. The observed trend was rationalized on the basis of both acid strength and size of the halogen.

The halogenation of $(CH_3)_3NBH_3$ by HX is reasonably viewed as a hydride abstraction involving the interaction of the B-H bond and HX to produce hydrogen gas and a B-X bond. On this basis, the strongest acid of the HX series, HI, should achieve halogenation or should accomplish a hydride abstraction to form H_2 and give $(CH_3)_3NBH_2X$ the most rapidly. The reactivity of HX towards $(CH_3)_3NBH_3$ should also decrease as the acid stength of HX decreases. With the exception of HF, the observed trend in the order of reactivity of HX towards $(CH_3)_3NBH_3$ is in accord with this rationalization. The smaller size of the fluoride ion compared to the chloride ion as the incoming nucleophile may be sufficient to overcome the weaker acid strength of HF, as compared to HCl, and to place it ahead of HCl in order of reactivity.

The monohalogenation of $(CH_3)_3NBH_3$ by all of the hydrogen halides was readily accomplished. However, the monohalogenated trimethylamine-borane, $(CH_3)_3NBH_2X$, where X = Cl or Br, has been found unreactive towards an excess of HX. For the adduct where X = I,

dihalogenation has been achieved using HI but at the condition of refluxing toluene[4]. The hydrogen halides are, therefore, selective halogenating agents towards $(CH_3)_3NBH_3$ and have made the preparation of $(CH_3)_3NBH_2X$, where X = Cl, Br, or I, very easy.

The inability of HX to further react with $(CH_3)_3NBH_2X$ when X = Cl, Br, or I at room temperature has been rationalized on the basis of a decreased hydridic character of the B-H bond. In other words, the electron density of the B-H bond has been decreased or inductively lowered by the electron withdrawing ability of the electronegative substituent, X. This effect should have been the least for $(CH_3)_3NBH_2I$, since iodine is the least electronegative of the halogens considered. Indeed, dihalogenation was found for $(CH_3)_3NBH_2I$ using HI, but only at elevated temperatures.

On the basis of lower hydridic character of remaining B-H bonds in a compound of the type $(CH_3)_3NBH_2X$, $(CH_3)_3NBH_2F$ should have been the least reactive toward further fluorination by HF since it was the most electronegative of the halogen substituents. However, $(CH_3)_3NBH_2F$ was found to be nearly as reactive as $(CH_3)_3NBH_3$ towards excess HF as it readily formed $(CH_3)_3NBHF_2$.

Trimethylamine-fluoroborane was also found to be reactive towards the other hydrogen halides forming trimethylamine-halofluoroboranes, $(CH_3)_3NBHXF$, where X = Cl, Br, or I. Qualitative observations of the reaction of HX towards $(CH_3)_3NBH_2F$ indicated the same approximate order of reactivity as HX towards $(CH_3)_3NBH_3$. The reaction of $(CH_3)_3NBH_2F$ with HI appeared to take place most

rapidly, and even though the reaction of $(CH_3)_3NBH_2F$ with HCl was fast, it was comparatively the slowest.

Therefore, it has been observed that the reactivity of $(CH_3)_3NBH_2F$ is similar to that of $(CH_3)_3NBH_3$ towards HX, where X = F, Cl, Br, or I. The fact that the reactivity of $(CH_3)_3NBH_2F$ towards HF was nearly the same as $(CH_3)_3NBH_3$ towards HF made $(CH_3)_3NBH_2F$ the most difficult to prepare of the monohalo derivatives of $(CH_3)_3NBH_3$. For the preparation of $(CH_3)_3NBH_2F$, the hydrogen halide, HF, was not a selective halogenating agent since even a slight excess of HF caused further fluorination.

The hydridic nature of a B-H bond in $(CH_3)_3NBH_3$, then, seems to be only slightly reduced by a fluorine substitution in the borane portion of the adduct, even though the substituent is highly electronegative. It would appear that its withdrawing inductive effect is sufficiently countered to leave the net electron density in the B-H bond essentially unchanged. Of the halogens, fluorine is the most able, and is known to engage in pi-bonding with the vacant p_z orbital of boron by using a non-bonding pair of its electrons.[25] The pi-bonding ability of fluorine to boron can return electron density to boron, thereby opposing the inductive effect of fluorine. Brown, Drago, and Bolles[26] state that possible pi-bonding in a BX_3 species is not destroyed but only reduced on coordination to an amine. The vacant p_z orbital of boron is available for electron density as donated by the lone pair of the nitrogen in the amine or as received

by a pi-interaction with fluorine. The only slight change in reactivity for the remaining B-H bonds on fluorine substitution in $(CH_3)_3NBH_3$ could also be accounted for by the fact that fluorine makes relatively little steric imposition on the molecule. Its similarity in size to hydrogen allows its replacement of hydrogen to be sterically unnoticed[27].

The reactivity of $(CH_3)_3NBH_2F$ was utilized to prepare the mixedhaloborane adducts of trimethylamine, $(CH_3)_3NBHXF$, where X = Cl, Br, or I, by reacting $(CH_3)_3NBH_2F$ with the appropriate HX. Trimethylamine-bromofluoroborane and trimethylamine-chlorofluoroborane were synthesized in high yield at ordinary conditions. Trimethylamine-fluoroiodoborane was prepared in high yield, but was not isolated.

In general, the reaction of $(CH_3)_3NBH_2F$ with HX occurred to give products of halogenation rather than a reaction involving an exchange of halogens. For example, the reaction of $(CH_3)_3NBH_2F$ with HCl resulted in $(CH_3)_3NBHClF$ rather than $(CH_3)_3NBH_2Cl$. The B-H bond appeared to be more reactive than the B-F bond in $(CH_3)_3NBH_2F$. However, the B-H bond which remained in the dihalo product had decreased in reactivity so that further halogenation by HX, where X = Cl, Br, or I, in the reaction mixture did not occur.

The trimethylamine-halofluoroboranes, $(CH_3)_3NBHClF$, $(CH_3)_3NBHBrF$, and $(CH_3)_3NBHIF$, were unreactive to HX, where X = Cl, Br, or I. However, they were reactive towards HF. The reaction resulted in a difluoro species which indicated that a reaction to effect an

exchange of halogen had occurred rather than a halogenation reaction which would have resulted in a trihalo species. For example, the reaction of HF on $(CH_3)_3NBHClF$ was found to give $(CH_3)_3NBHF_2$ rather than $(CH_3)_3NBClF_2$. Therefore, in the species $(CH_3)_3NBHXF$ the B-X bond was more reactive than the B-H bond towards HF. The introduction of X into $(CH_3)_3NBH_2F$, where X = Cl, Br, or I, apparently sufficiently decreased the reactivity of the remaining B-H bond so that it was no longer reactive. Both the inductive effect of X and the steric nature of X functioned to make the remaining B-H bond of $(CH_3)_3NBHXF$ less susceptible to attack by HX. However, the reaction of $(CH_3)_3NBHF_2$ with HF quickly achieved halogenation of the remaining B-H bond to give $(CH_3)_3NBF_3$. Two fluoro substituents did not either sterically or electronically impair the reactivity of the remaining B-H bond.

It has been noted that $(CH_3)_3NBHF_2$ required handling in inert conditions in order to avoid ammonium salt formation. The mixed dihaloborane adducts of trimethylamine were also prone to instability with a reactivity order of:

$$(CH_3)_3NBHIF \succ (CH_3)_3NBHBrF \succ (CH_3)_3NBHClF$$

Trimethylamine-chlorofluoroborane could be handled in the laboratory atmosphere, but exposure was kept to a minimum. Trimethylamine-bromofluoroborane fumed on exposure to room conditions and therefore was handled in a dry box to avoid ammonium salt formation. The ^1H nmr spectra of a CH_2Cl_2 solution of $(CH_3)_3NBHIF$ showed that a small amount of ammonium salt had formed, as indicated by the

characteristic small doublet near 170 Hz, while it remained at room temperature for several days. However, ^1H nmr spectra of a CH_2Cl_2 solution of $(CH_3)_3NBHIF$ showed at these conditions that $(CH_3)_3NBHIF$ was unstable primarily with respect to disproportionation. After several days, the disproportionation of $(CH_3)_3NBHIF$ was complete to give $(CH_3)_3NBF_3$, $(CH_3)_3NBHI_2$ and $(CH_3)_3NBH_2I$.

Of the mixed adducts, $(CH_3)_3NBHXF$, only $(CH_3)_3NBHIF$ was found reactive towards $(CH_3)_3N$ to form the cationic species, $((CH_3)_3N)_2BHF^+$ which precipitated from a benzene solution as the iodide salt. Trimethylamine did not react with $(CH_3)_3NBHBrF$. It has been reported that for adducts of the type, $(CH_3)_3NBH_2X$, $(CH_3)_3NBH_2I$ readily forms a cation with $(CH_3)_3N$ whereas $(CH_3)_3NBH_2Br$ does not[7,4]. A recent mass spectral study has indicated that the B-X bond is weakened as X becomes a heavier halogen[6]. In the series, $(CH_3)_3NBHXF$, only the B-I bond appeared sufficiently weak to involve displacement of a halide substituent by $(CH_3)_3N$.

It has been noted that the chloro, bromo, or iodo derivative of $(CH_3)_3NBH_3$ is not reactive to HCl, HBr, or HF at ordinary conditions. However, these adducts were reactive towards HF with respect to halogenation to form the species $(CH_3)_3NBHXF$, where X = Cl, Br, or I. Even though the B-H bond in $(CH_3)_3NBH_2X$ is of reduced reactivity, HF in contrast to the other hydrogen halides was a successful halogenating agent. Hydrogen fluoride has the advantage of its small size to bring it closer to the reaction site in addition to the accompanying formation of a B-F bond which

has been indicated to be a very favorable process due to the high B-F bond strength[25]. However, the synthesis of the mixed dihalo adducts, $(CH_3)_3NBHXF$, using the reaction of $(CH_3)_3NBH_2X$, and HF was not convenient, since the initial product, $(CH_3)_3NBHXF$ rapidly exchanged B-X for B-F by means of the HF to form $(CH_3)_3NBHF_2$. The nmr spectra of the reaction solution showed the presence of $(CH_3)_3NBHF_2$ as soon as some $(CH_3)_3NBHXF$ had formed. The $(CH_3)_3NBHF_2$ subsequently reacted with HF to give the final product of the reaction, $(CH_3)_3NBF_3$. Trimethylamine-difluoroborane, $(CH_3)_3NBHF_2$, did not react with any of the other hydrogen halides.

Trimethylamine-fluoroborane and trimethylamine-difluoroborane were found to be readily and completely halogenated by Cl_2 and Br_2. Successive chlorination and bromination resulted in the following mixed trihalo species: $(CH_3)_3NBCl_2F$, $(CH_3)_3NBClF_2$, $(CH_3)_3NBBr_2F$, and $(CH_3)_3NBBrF_2$. Both halogenations were achieved at ordinary conditions. For the halogenation of $(CH_3)_3NBH_2F$, the intermediate, $(CH_3)_3NBHXF$, where X = Cl or Br, was the first product of the halogenation as observed in the nmr spectrum. The nmr spectrum indicated the halogenation of $(CH_3)_3NBH_2F$ to be a stepwise process with the intermediate experimentally separable if the amount of halogen used was the stoichiometric amount required to achieve the desired extent of halogenation.

Iodination of $(CH_3)_3NBH_2F$ was attempted using I_2, but it was unsuccessful. The products of the reaction could be best accounted for by subsequent reaction of HI, a product of the

initial iodination, with $(CH_3)_3NBH_2F$ to give a rapid exchange of halogen so that $(CH_3)_3NBH_2I$ and HF were formed. The HF further fluorinated the remaining starting material to finally form $(CH_3)_3NBF_3$. The reaction of HI and $(CH_3)_3NBH_2F$ was shown in a separate experiment to be extremely fast. In order to avoid the side reactions caused by the presence of HI, the reaction was done in the presence of known acceptors of HI such as triethylamine, di-isopropylamine, 2,4,6-tri-tertbutylamine, or cyclohexene. However, the products of the reaction were unchanged. It appeared that neither of these substances could effectively compete with $(CH_3)_3NBH_2F$ for HI.

The use of exchange reactions to produce mixed halo derivatives of trimethylamine-borane proved not to be successful as a general synthetic approach. Exchange reactions were found to occur but were not predictable and were difficult to control. For example, the reaction of HF with $(CH_3)_3NBCl_3$ to accomplish an exchange of F for Cl resulted in $(CH_3)_3NBF_3$ as the only observable product in the ^1H nmr spectrum. Also, the preparation of $(CH_3)_3NBBrClF$ was attempted using the reaction of $(CH_3)_3NBBr_2Cl$ and a stoichiometric amount of HF contained in a CH_2Cl_2 solution of HF. However, no exchange of Br for F was observed. Anhydrous HF was then passed through the solution but $(CH_3)_3NBF_3$ was the only resulting product. No synthetic route to mixed haloborane adducts of trimethylamine utilizing an exchange process was found.

Mixed halo derivatives of trimethylamine-borane were, however,

shown to be easily prepared and in all varieties by employing the appropriate direct halogenation. For example, $(CH_3)_3NBBrClF$ was synthesized by successive fluorination, chlorination, and bromination of $(CH_3)_3NBH_3$ as shown by equations 3-1, 3-4, and 3-10.

$$(CH_3)_3NBH_3 + HF \rightarrow (CH_3)_3NBH_2F + H_2 \quad (3\text{-}1)$$

$$(CH_3)_3NBH_2F + HCl \rightarrow (CH_3)_3NBHClF + H_2 \quad (3\text{-}4)$$

$$(CH_3)_3NBHClF + Br_2 \rightarrow (CH_3)_3NBBrClF + H_2 \quad (3\text{-}10)$$

The syntheses developed in this work support an earlier observation that halogen substitution on $(CH_3)_3NBH_3$ to give mixed halo derivatives must be in the order of decreasing electronegativity of the halogen.[4] In this work, chlorination or bromination had to follow fluorination. Fluorination of a partially halogenated amine-borane resulted in exchange of fluorine for halogen rather than fluorination of a B-H bond.

The syntheses of fluorosubstituted trimethylamine-boranes are summarized schematically in Figure 4-1.

Information relating to reactivities and further characterization of the entire family of fluorosubstituted trimethylamine-boranes was obtained from both the nmr spectra and infrared. The nmr spectra were particularly useful since the adducts in this work had three nuclei, namely, ^1H, ^{11}B, and ^{19}F, on which nuclear magnetic resonance could be done. The ^1H, ^{11}B, and ^{19}F nmr spectra were interesting in themselves for the trends in spectral properties which were observed for the series of fluorinated borane

adducts of trimethylamine. The various nmr spectra and the trends which they developed were used in making correlations concerning bonding within the adduct, particularly the borane portion, and the relative strength of the fluoro- and fluorohaloboranes as Lewis acids towards trimethylamine. Both the ^{11}B and ^{19}F spectra were of immediate use in the identification of the adducts as they were prepared.

The chemical shift in the ^{1}H nmr spectra for the methyl resonance of the trimethylamine-fluoroboranes and the trimethylamine-fluorohaloboranes are given in Table 4-1. The methyl resonance for the BH_3, BH_2X, BHX_2, and BX_3 adducts of trimethylamine, $(CH_3)_3N$, where X = F are displayed and compared to the methyl resonance for the adducts of $(CH_3)_3N$, where X = Cl, Br, or I, in Figure 4-2.

As the degree of halogenation increases from the adduct of BH_3 to the adduct of BX_3, the chemical shift for the methyl resonance is observed at lower field. The methyl protons become more de-shielded as successive chlorination or bromination occurs in the borane portion of the molecule. A downfield displacement of the chemical shift occurs not only as the number of halogens is increased, but also as their size is increased. The shift of the methyl resonance downfield from that of the methyl resonance in $(CH_3)_3NBH_3$ is greater for dihalo substitution than monohalo substitution, and greater for bromination than chlorination. These trends have recently been well explained

for derivatives not containing fluorine, on the basis of steric interference between the halogens and the methyl protons of the amine.[27] The trend observed for the fluorinated adducts is in accord with the size of the halogen substituent. Fluorine, the smallest of the halogens, would be expected to give the least steric interference to the methyl protons, and thereby produce the least downfield shift. However, in the series of fluorinated borane adducts of trimethylamine, the chemical shift shows a slight upfield trend as the number of fluorine substituents are increased to give mono- and di-substitution. This at least indicates that a steric factor is not solely responsible for determining the chemical shift of these adducts in the ^1H nmr. Electronic factors and magnetic anisotropy can contribute to the observed chemical shift.

Since magnetic anisotropy in the boron-halogen bond can produce small upfield shifts in the ^1H nmr, it must be considered as an influential contribution to the chemical shift for the fluorine-containing adducts. The upfield trend resulting from magnetic anisotropy would counter the trend produced sterically in the halogenated trimethylamine-boranes. The trend for the methyl resonance which is observed for the chloro-, bromo-, and iodoborane adducts of $(CH_3)_3N$ is that which would be established by the steric interference factor. In these halogenated adducts, the bulk of the halogen is sufficient to override a magnetic anisotropic factor. However, for the fluorosubstituted borane adducts, the

comparatively small size of the fluorine has much less steric influence on the methyl proton of the amine. The steric influence on the methyl proton of the amine is enough less than for the other halogens so that the magnetic anisotropy of the B-X bond is not countered. Instead, the upfield trend as suggested by magnetic anisotropy is observed in the ^1H nmr spectrum for the methyl resonance of $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$. The chemical shift for the methyl proton of $(CH_3)_3NBF_3$ is the same as for the unhalogenated amine-borane. It appears that three fluoro substituents provide a steric influence to counter the upfield shift caused by magnetic anisotropy, to the extent that the shift is returned to that of $(CH_3)_3NBH_3$. It would appear from these observations that substitution of fluorine for hydrogen in the borane portion of $(CH_3)_3NBH_3$ is sterically "unnoticed".

There is little difference in the chemical shift for the methyl resonance between the bromoborane and the bromofluoro adducts of trimethylamine as shown by the following data and Figure 4-2.

$(CH_3)_3N$ adduct	BH_2Br	BF_2Br	$BHBr_2$	$BFBr_2$
Hz	163	164	174	174

Changing the smaller, similar substituents, hydrogen and fluorine, in these adducts does not alter the steric influence which the larger bromine substituent establishes on the methyl protons. In the same comparison for chloroborane and chlorofluoroborane adducts of trimethylamine, the steric influence of chlorine is less overwhelming so that the presence of hydrogen or fluorine makes

a difference in the chemical shift.

$(CH_3)_3N$ adduct	BH_2Cl	BF_2Cl	$BHCl_2$	$BFCl_2$
Hz	158	163	163	170

The trends in the chemical shift for ^1H, ^{11}B, and ^{19}F as established by halogen substitution show that the largest increment of change occurs on proceeding from fluorine to chlorine in the halogen family. The increment of change is less going from chlorine to bromine. An example of this is seen in the chemical shift for the methyl proton of the following adducts.

$(CH_3)_3N$ adduct	BF_3	BF_2Cl	BF_2Br	
Hz	157	163	164	
		$BFCl_2$	$BFBr_2$	BFBrCl
		170	174	173

A larger difference on substituting chlorine for fluorine than on substituting bromine for chlorine reflects a general trend in the halogen family. The greatest difference in periodic properties is between fluorine and chlorine, that is, chlorine is more like bromine than it is like fluorine.

The difference in the chemical shift of the methyl resonance of trimethylamine and the borane adduct of trimethylamine has been referred to as complexation shift[28]. It has been quoted by some[5,28] authors as an approximate measure of the bond strength of the adduct. A greater change in downfield shift of the methyl proton is considered to indicate a stronger donor-acceptor interaction. For example, the downfield shift of the methyl resonance

of the trimethylamine adducts of the boron trihalides is greatest for the strongest acid, BI_3.

The acidity of the boron trihalides towards a given donor is dependent on the ability of the vacant $2p_z$ orbital of boron to accept electron density from the donor. In formation of the adduct, $(CH_3)_3NBX_3$, there is competition between the electron density from the pi-bonding ability of X and the donating ability of the amine. The pi-bonding ability of X decreases in the following order: $F \gg Cl > Br > I$. Since fluorine is best able to pi-bond to boron, the p orbital of boron in BF_3 is less available for electron density from the amine than in the other boron trihalides. The relative acidity of the boron trihalides towards trimethylamine parallels the extent of pi-bonding in the borane. The observation that the complexation shift is least for $(CH_3)_3NBX_3$, where X = F, is rationalized on the basis that this is the weakest donor-acceptor interaction of the boron trihalides, since BF_3 is the poorest acid.

Since it is the acidity of the $2p_z$ orbital on boron, or rather, its availability to donate electron density that determines the relative Lewis acidity of a borane, the Lewis acidity of a boron trihalide should increase as fluorine substitution decreases. As the number of fluorines decreases, the availability of the acceptor orbital of boron should increase and hence its acidity. According to the idea of complexation shift, a decrease in the number of fluorines in the borane portion of the trimethylamine adduct should be accompanied by a larger downfield shift for the

methyl resonance. The following data indicate such a trend.

$(CH_3)_3N$ adduct	BF_3	$BClF_2$	BCl_2F	BCl_3
Hz	157	163	170	179
		$BBrF_2$	BBr_2F	BBr_3
		164	174	187
			BBrClF	
			173	

The chemical shifts of the methyl proton in these trimethylamine adducts are nearly identical for the same number of fluorines. It should be noted, however, that the downfield shift observed for these adducts also correlates with the principle of increased steric interference for the methyl protons as the number and size of halogens is increased in the borane portion of the adduct.

The expected downfield trend in the methyl resonance for the mixed dihalo adducts of trimethylamine is shown by the following data.

$(CH_3)_3N$ adduct	BHClF	BHBrF	BHIF
Hz	156	161	156

These adducts show a slight upfield shift in methyl resonance from that of the monohaloborane adduct.

$(CH_3)_3N$ adduct	BH_2Cl	BH_2Br	BH_2I
Hz	158	163	169

On the basis of complexation shift, the fluorohaloborane is a weaker acid relative to the monohaloborane towards trimethylamine. The fluorine substituent reduces slightly the acidity of the vacant p orbital on boron due to its ability to involve this orbital in pi-bonding.

Both the ^{19}F and ^{11}B nmr spectra were useful in identifying the stoichiometries of trimethylamine-fluorosubstituted boranes as they were prepared. The multiplicity and intensity of the resonances observed in both the ^{19}F and ^{11}B spectra for all adducts synthesized were as expected for the stoichiometry. For a given stoichiometry, the nmr spectrum was predicted on the basis of interaction of nuclear spin and the consideration of the magnitude of the appropriate coupling constants. As an example of this, an analysis of the ^{19}F and ^{11}B nmr in the support of $(CH_3)_3NBHIF$ was given in Chapter 3. As shown by the following data, a coupling constant common to both ^{19}F and ^{11}B nmr spectra was found to be of the same value in either spectrum.

	$(CH_3)_3NBHClF$	$(CH_3)_3NBHBrF$	$(CH_3)_3NBHIF$
J_{BF} in ^{19}F	82	88	94
J_{BF} in ^{11}B Hz	82	88	92

The chemical shifts for the ^{19}F resonance, the hydrogen-fluorine coupling constant, J_{HBF}, and the boron-fluorine coupling constant, J_{BF}, for the trimethylamine-fluorosubstituted-boranes are given in Table 4-2. The chemical shifts for the ^{19}F resonance of both the free mixed boron trihalides[29] and the trimethylamine adducts of the mixed boron trihalides are shown graphically in Figure 4-3.

The trend for the trimethylamine adducts of the mixed boron trihalides is similar to that which has previously been observed in the free mixed boron trihalides.[29] A downfield shift is

observed for the ^{19}F resonance of the adduct as fluorine substitution decreases. The downfield shift increased as the number and size of the other halogen substituent increased.

On the basis of the known ability of fluorine to engage in p-pi-p-pi-bonding to boron by using one of its non-bonding pairs of electrons to back-donate to the vacant 2p orbital on boron, one can predict a downfield shift in the ^{19}F resonance as fluorine in BF_3 is replaced by substituents less capable of pi-bonding. This prediction is based on the relative change in electron density at the fluorine atom which is caused by the change in the amount of pi-bonding for the fluorine. Of the halogens, fluorine is the best able to pi-bond to boron, so that BF_3 has the maximum amount of pi-bonding for a boron trihalide.[25,30] The total amount of pi-bonding is equally distributed among the three fluorines. If one of the fluorines is replaced by another halogen, the pi-bonding for the molecule is no longer partitioned among three fluorines, but two fluorines, so that the pi-bonding per fluorine is increased. The extent of back-donation of electron density for the fluorine to boron pi-system increases per fluorine. The increased pi-bonding per fluorine is accompanied by a decreased electron density at the fluorine atom, which is realized as a de-shielding of the ^{19}F nucleus in the nmr spectrum. The ^{19}F nmr spectrum should therefore show the ^{19}F resonance for BF_2Cl at a lower field than BF_3. The shift in the ^{19}F resonance should be farther downfield if

fluorine is substituted by bromine rather than chlorine, since bromine is much less capable of pi-bonding than chlorine.

Therefore, on the basis of increased pi-bonding per fluorine. a downfield shift should be observed for the ^{19}F resonance as the fluorine in BF_3 is successively substituted by other halogens of increasing size. This predicted order of downfield shift from BF_3 for the ^{19}F resonance of free boron trihalides is observed.[29] The order of increasing downfield shift from BF_3 is as follows:

$$BF_2Cl < BF_2Br < BFCl_2 < BFClBr < BFBr_2$$

The same order is observed in the ^{19}F nmr spectra for the trimethylamine adducts of these Lewis acids. The similarity in trend for the ^{19}F resonance of the trimethylamine adducts of the boron mixed trihalides to that of the free boron mixed trihalides would suggest that the pi-bonding in the borane is only reduced rather than destroyed on adduct formation. Even though coordination of BX_3 decreases the availability of the vacant 2p orbital for pi-bonding in the borane, pi-bonding can still exist in the borane portion of the adduct. Brown, Drago, and Bolles[26] have discussed this in terms of a residual pi-bonding that remains in the borane portion of the adduct effectively competing with electron density from the donor atom.

If the fluorine chemical shift is plotted against the difference in chemical shift for the adduct and free trihalide as in Figure 4-4, a straight line is observed. The explanation for the downfield trend in ^{19}F resonance as the trifluoro species

is substituted by halogen is based on the assumption that the amount of pi-bonding remains unchanged, so as the number of fluorines decreases, the amount of pi-bonding per fluorine increases. On this basis also, it is expected that the greatest change on adduct formation would occur for the species which has the greatest amount of pi-bonding per fluorine, namely, $BFBr_2$. Figure 4-4 shows that the greatest change in downfield shift for the fluorine resonance occurs for the $BFBr_2$ adduct.

In consideration of the electron density at the fluorine atom as reflected by the fluorine resonance in the nmr spectra for the various mixed boron trihalides and their trimethylamine adducts, attention has been focused on the pi-system. Even though it is this system that correlates the observed trend, it is the combined effect of the sigma- and pi-system that determines the electron density at fluorine. If the sigma-system alone determined the bonding, a greater downfield shift for a chlorine substituent than for a bromine substituent would be expected, since chlorine is the more electronegative. However, the ^{19}F chemical shift is greater for the adduct containing a bromine substituent than for the adduct containing a chlorine substituent. The greater downfield shift for bromine substitution indicates that the influence of the pi-system is significant enough to counter that of the sigma-system, and to determine the observed trend. This observation then indicates that even though chlorine has poorer pi-bonding ability than fluorine, it has a better pi-bonding ability than bromine.

In contrast to the ^{19}F nmr for $(CH_3)_3NBX_{3-n}F_n$ species, the data show an upfield shift from $(CH_3)_3NBF_3$ for the fluorine resonance of $(CH_3)_3NBHF_2$ and $(CH_3)_3NBH_2F$.

$(CH_3)_3N$ adduct	BF_3	BF_2H	BH_2F
ppm from C_6F_6	-1.2	-0.7	+40.8

This trend can also be rationalized on the basis of the change in pi-bonding per fluorine. For comparison to the trihaloborane adducts, $(CH_3)_3NBHF_2$ is considered the result of a hydride substitution on $(CH_3)_3NBF_3$. A hydride substituent is a better sigma-donor than a fluorine substituent, but it has a much poorer pi-bonding ability than fluorine. Compared to a fluorine substituent, the net result of the sigma- and pi-bonding of a hydride would be an increase in the electron density at boron. An increase in electron density on the boron atom would result in less pi-bonding for the remaining fluorines. A decrease in the amount of pi-bonding per fluorine is accompanied by an increase in electron density at fluorine which is reflected in the fluorine resonance as an upfield shift from $(CH_3)_3NBF_3$.

The hydrogen-fluorine coupling constant, J_{HBF}, and boron-fluorine coupling constant, J_{BF}, as observed in the ^{19}F nmr spectra, are given in Table 4-2. It is observed that the $J_{BF} = 0.5J_{HBF}$ for $(CH_3)_3NBH_2F$, and that the $J_{BF} = J_{HBF}$ for $(CH_3)_3NBHF_2$.

$(CH_3)_3N$ adduct	BHF_2	BH_2F
J_{BF} Hz	71	90
J_{HBF} Hz	71	45

Heitsch[13] has also observed that two or more spin couplings which

involve the same atom are often integral multiples.

A linear correlation between ^{19}F chemical shift and coupling constant, J_{BF}, has been observed for the free boron mixed trihalides[31]. Figure 4-5 shows that a similar correlation is also obtained for the trimethylamine adducts of these boron trihalides. The magnitude of the J_{BF} is observed to increase as the pi-bonding per fluorine or strength of the boron-fluorine interaction is increased as a result of substituent changes.

The mixed dihaloborane adducts also show an increased J_{BF} which correlates well with the increased pi-bonding per fluorine as the other halogen substituent in the series becomes less capable of pi-bonding.

$(CH_3)_3N$ adduct	BHFCl	BHFBr	BHFI
J_{BF} Hz	82	88	94

The decreased electron density at fluorine in the above series, $(CH_3)_3NBHX$, is accompanied by an increase in electron density at boron as expected and as shown in the data from the ^{11}B spectra.

$(CH_3)_3N$ adduct	BHFCl	BHFBr	BHFI
ppm from $B(OCH_3)_3$	+12.1	+13.3	+16.1

The ^{11}B chemical shift for these adducts shows an increasing electron density at boron as reflected by an increase in the upfield shift of the boron resonance.

The chemical shifts for the ^{11}B resonance, the boron-hydrogen coupling constant, J_{BH}, and the boron-fluorine coupling constant, J_{BF}, as observed in the ^{11}B nmr spectra for the trimethyl-

amine-fluorosubstitutedboranes are given in Table 4-3. The chemical shifts for the ^{11}B resonance is the net result of changes in the amount of electron density received by the vacant 2p orbital of boron from the trimethylamine and from the pi-bonding of the substituents and changes in the sigma-bonding of the borane on formation of the adduct. The changes in electron density at the boron atom in fluorosubstitutedborane adducts of trimethylamine is not as regularly accounted for as changes in electron density at the fluorine atom.

Figure 4-6 shows graphically the relationship between the chemcial shift for the ^{11}B resonance of the adduct and the difference in chemical shift for the ^{11}B resonance of the adduct and the free boron trihalide. It is observed that the change in ^{11}B chemical shift on adduct formation is similar for the boron trihalides having the same number of fluorines. Figure 4-6 is similar to the plot, Figure 4-4, made for the data in the ^{19}F nmr spectra. However, on coordination of the free boron trihalide to trimethylamine, an upfield shift is observed in the ^{11}B resonance. As for the ^{19}F spectra, the greatest change in chemical shift on adduct formation occurs for $BFBr_2$. In the ^{11}B nmr spectra, this change is observed as an upfield shift in the ^{11}B resonance for $BFBr_2$. It is also noted that the change in ^{11}B chemical shift on adduct formation is similar for the boron trihalides having the same number of fluorines.

An attempt has been made by Spielvogel and Purser[32] to correlate the ^{11}B chemical shifts with the substituents on boron.

The correlation was based on the additivity of pairwise interaction parameters as had been done earlier by Malinowski[33] and co-workers to account for ^{13}C shifts in substituted methanes. The rule of pairwise additivity for a tetra-coordinated resonance nucleus is that the chemical shift is equal to the sum of the pairwise additivity parameters, $n_{i,j}$, that have been established for the six pairs of interactions that arise from the four substituents. For example, the ^{11}B chemical shift for $(CH_3)_3NBF_3$ was calculated as the sum of three $(CH_3)_3N,F$ interactions, and three F,F interactions as +18.0 ppm from $BF_3 \cdot (C_2H_5)_2O$. The observed was +17.9 ppm. Some of the interaction parameters for ^{11}B required calculation from ^{13}C data. Using both known and derived ^{11}B pairwise interaction parameters, chemical shifts were calculated for the fluorosubstituted borane adducts of trimethylamine. The calculated chemical shifts, however, did not compare was well to the observed shifts as the examples which are cited in the literature for other substituted amine-boranes. For example, the calculated ^{11}B chemical shift for $(CH_3)_3NBH_2F$ was 9.0 ppm upfield from $B(OCH_3)_3$, whereas the observed ^{11}B chemical shift was 14.9 ppm upfield from $B(OCH_3)_3$

The difference in chemical shift of the trimethylamine adduct and the free boron trihalides as observed for the fluorine resonance in the ^{19}F nmr spectra is plotted against the difference as observed for the boron resonance in the ^{11}B nmr spectra, in Figure 4-7. It will be noted that a linear correlation exists, and that the data points are arranged by the number of fluorine substituents.

The infrared spectra for the fluorosubstituted trimethylamines synthesized in this work are described in Table 3-1 and shown appropriately in Chapter 3. The infrared spectra are especially informative with regard to the borane portion of the adduct. The most revealing portion of the spectra is the frequency attributed to the symmetric and asymmetric stretching of the B-H bond.

It has been stated by Wiggins[19] and Mathur[4] that as $(CH_3)_3NBH_3$ is successively substituted with chlorine or bromine, the B-H stretch is shifted to higher frequencies, suggesting a removal of electron density from the hydrogen. Therefore, the hydrogen becomes less hydridic as the B-H stretch shifts to a higher wave number. Wiggins[19] has reported the following data.

$(CH_3)_3N$ adduct	BH_3	BH_2Cl	$BHCl_2$
cm^{-1}	2260-2290	2340	2480

It has been shown that the reactivity of trimethylamine-haloboranes indicates a lesser hydridic character for the B-H bond than in $(CH_3)_3NBH_3$.

The following frequencies are observed for the trimethylamine-fluoroboranes.

$(CH_3)_3N$ adduct	BH_3	BH_2F	BHF_2
cm^{-1}	2360,2310, 2280,2260	2360 2290,2270	2400

The B-H stretching regions of $(CH_3)_3NBH_2F$ and $(CH_3)_3NBH_3$ appeared to be of very similar frequency. This was reflected in the similarity of reactivity for the B-H bond in $(CH_3)_3NBH_3$ and $(CH_3)_3NBH_2F$, as was discussed previously.

The B-H stretch for a given $(CH_3)_3NBHX_2$ should be the highest for the adduct where X = F, since the withdrawal of electron density from hydrogen should be greatest for the most electronegative of the halogens. The data for the series indicate instead that the B-H stretch for $(CH_3)_3NBHF_2$ is the lowest.

$(CH_3)_3N$ adduct	BHF_2	$BHCl_2$	$BHBr_2$	BHI_2
cm^{-1}	2400	2480	2510	2525

(Data for BHF_2 from this work. Data for $BHCl_2$ from reference 19. Data for $BHBr_2$ and BHI_2 from reference 4.) The B-H stretching frequency for the series of $(CH_3)_3NBHX_2$ indicates that the net withdrawal of electrons for H is least for $(CH_3)_3NBHF_2$. Hence, an inductive effect due to electronegativity is not solely responsible.

A similar reversal of the order expected for the B-H frequency is observed in the data for the mixed dihalo adducts.

$(CH_3)_3N$ adduct	BHClF	BHBrF
cm^{-1}	2440	2450

However, the observed trend in the B-H frequencies can be accounted for if the bonding ability of the halogens is considered. It appears that the pi-bonding ability which is in the order

$$F \gg Cl > Br > I$$

is significant enough to counter the order of electronegativity and determine the trend of electron density in the B-H bond.

The shift of electron density is opposite that expected on the basis of electronegativity. This reversal can be accounted

for by the pi-bonding ability of the substituent. Alternatively the reversal could be accounted for on the basis of the steric influence of the substituents. As substituents increase in size, their accommodation around the boron atom will cause changes in bond angles for the substituents, that is, an alteration of the hybridization of the central atom, boron. Specifically, the change in hybridization of the boron will be towards increased p-character as substituents become bulkier. Increased p-character in boron could, for example, provide a better overlap of orbitals for the B-H bond. The resulting increase in bond strength would produce a higher stretching frequency in the infrared spectra. As shown by the data for the B-H stretching frequency in the series of adducts, $(CH_3)_3NBHX_2$, the B-H stretching frequency shifts to higher wave numbers, indicating a greater electron density for the bond, as X increases from fluorine to iodine. Therefore, steric considerations can also serve to correlate the infrared spectra of these adducts.

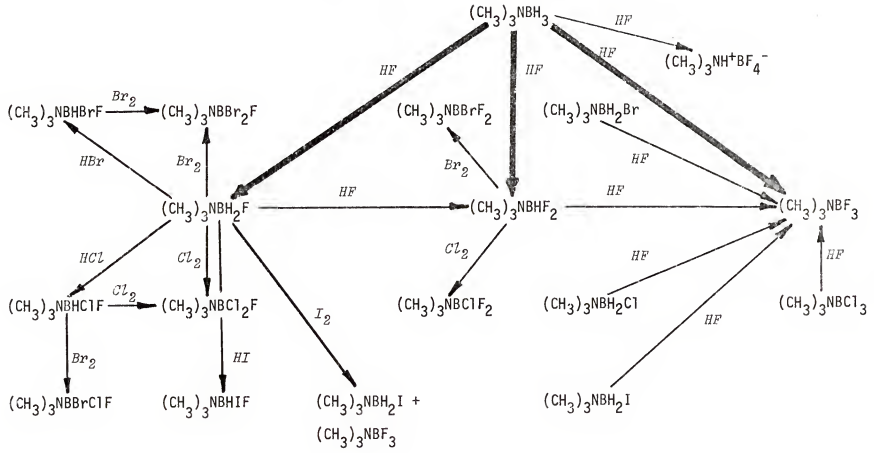

Figure 4-1. Scheme of syntheses of fluorosubstituted trimethylamine-boranes.

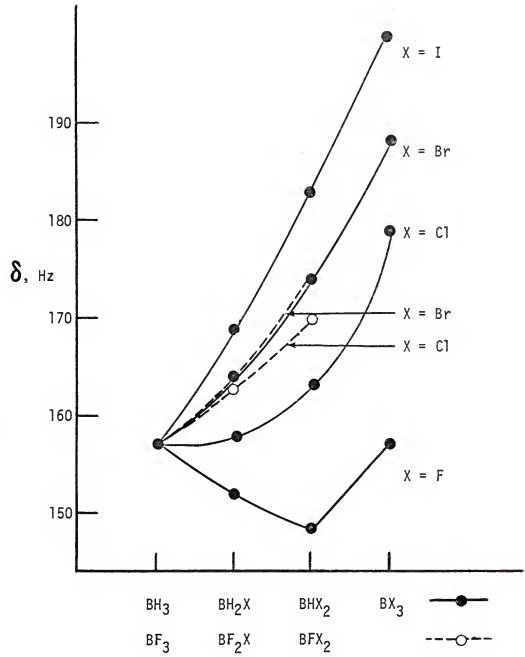

Figure 4-2. Chemical shift of methyl resonance of haloborane adducts of $(CH_3)_3N$ as a function of extent of halogenation and extent of fluorosubstitution.

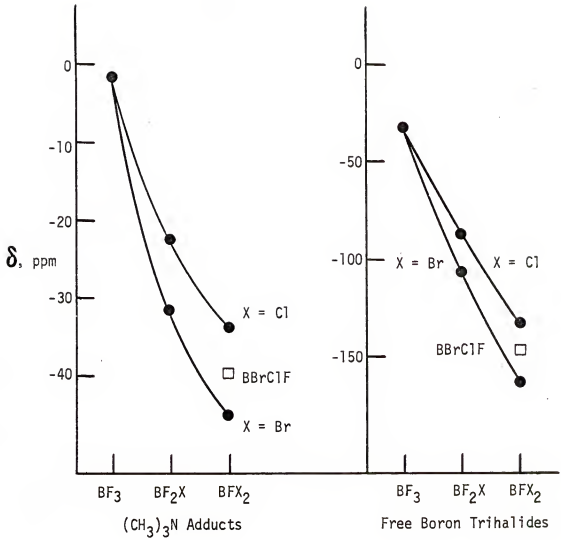

Figure 4-3. ^{19}F chemical shift for $(CH_3)_3N$ adducts of boron trihalides and free mixed boron trihalides as a function of number of fluoro substituents.

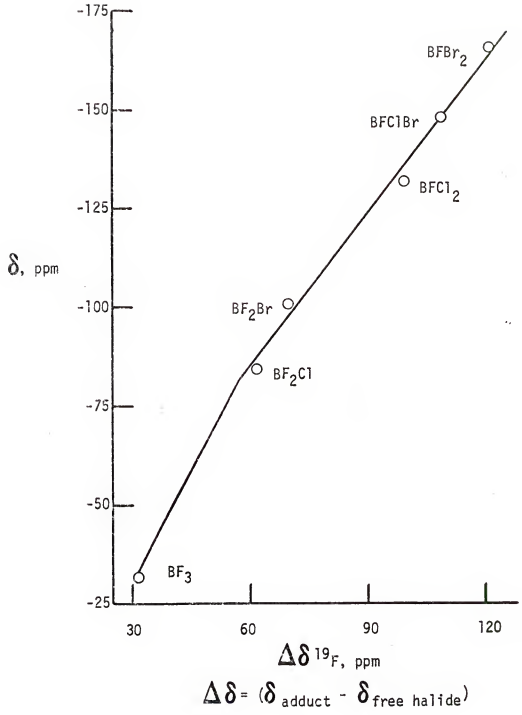

Figure 4-4. ^{19}F chemical shift of $(CH_3)_3N$ adducts of boron trihalides as a function of the difference in ^{19}F chemical shift for $(CH_3)_3N$ adduct and free boron trihalides.

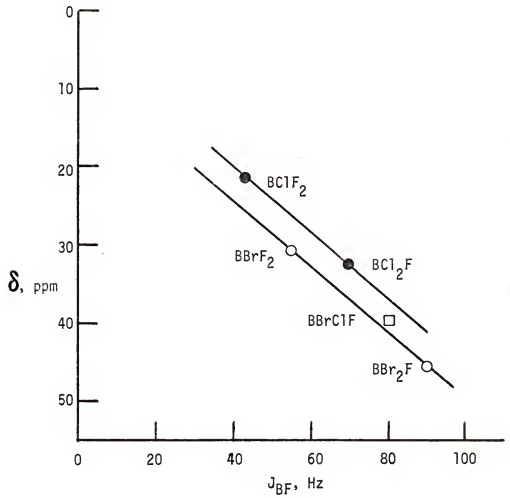

Figure 4-5. ^{19}F chemical shift of $(CH_3)_3N$ adducts of boron trihalides as a function of J_{BF}.

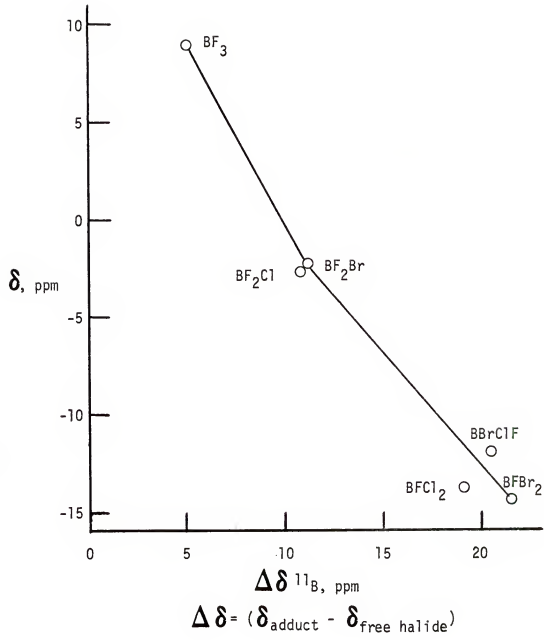

Figure 4-6. ^{11}B chemical shift of $(CH_3)_3N$ adducts of boron trihalides as a function of the difference in ^{11}B chemical shift for $(CH_3)_3N$ adduct and free boron trihalides.

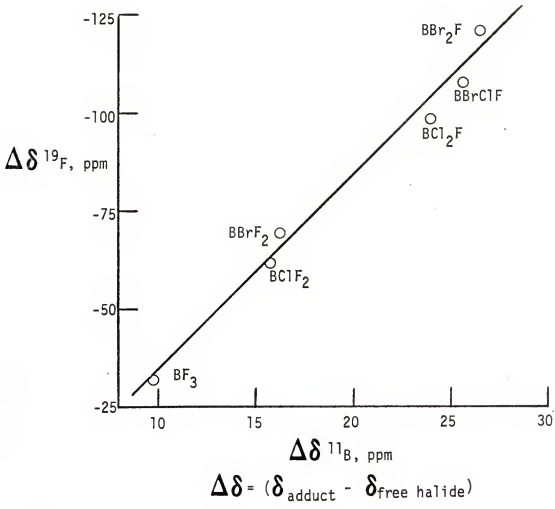

Figure 4-7. The difference of ^{19}F chemical shift of $(CH_3)_3N$ adduct and free borane as a function of difference of ^{11}B chemical shift of $(CH_3)_3N$ adduct and free borane.

Table 4-1

^1H NMR Data for $(CH_3)_3N$ Adducts

Solvent: CH_2Cl_2; Reference: Internal tetramethylsilane

Borane	δ_{CH_3}(Hz)	Multiplicity	J_{HCNB}(Hz)
BH_3	157	1	
BH_2F	152	1	
BHF_2	148	1	
BF_3	157	multiplet	
BHClF	156	1	
$BClF_2$	163	4	1.8
BCl_2F	170	4	2.1
BCl_3	179	4	2.8
BHBrF	161	1	
$BBrF_2$	164	4	
BBr_2F	174	4	2.9
BBr_3	187	4	3.1
BBrClF	173	4	2.5
BHIF	166	1	

Table 4-2

^{19}F NMR Data for $(CH_3)_3N$ Adducts

Solvent: CH_2Cl_2; Reference: External C_6F_6

Borane	δ(ppm)	Multiplicity	J_{BF}(Hz)	J_{HBF}(Hz)
BH_2F	+40.8	9	90	45
BHF_2	-0.7	5	71	71
BF_3	-1.2	4	15	
BHClF	-0.9	8	82	53
$BClF_2$	-22.6	4	43	
BCl_2F	-33.5	4	69	
BHBrF	-5.5	8	88	50
$BBrF_2$	-31.7	4	54	
BBr_2F	-45.0	4	89	
BBrClF	-39.3	4	79	
BHIF	-10.3	8	94	48

Table 4-3

^{11}B NMR Data for $(CH_3)_3N$ Adducts

Solvent: CH_2Cl_2; Reference: External $B(OCH_3)_3$

Borane	δ (ppm)	Multiplicity	J_{BH}(Hz)	J_{BF}(Hz)
BH_3	+26.3	4	98	
BH_2F	+12.9	6	115	90
BHF_2	+14.9	5	144	71
BF_3	+17.9			
BHClF	+12.1	4	155	82
$BClF_2$	+13.3	3		43
BCl_2F	+10.2	2		68
BHBrF	+13.3	4	160	88
$BBrF_2$	+14.1	3		54
BBr_2F	+15.2	2		86
BBrClF	+12.0	2		82
BHIF	+16.1	4	168	92

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BIOGRAPHICAL SKETCH

Jean Roselle Bergerud was born on May 1, 1943, in Fergus Falls, Minnesota. In June, 1961, she graduated from Northfield High School, Northfield, Minnesota. She attended St. Olaf College in Northfield and graduated as a chemistry major with a B. A. degree in May, 1965. From September, 1965 through May, 1968, she was a chemistry teacher at Wausau Senior High School, Wausau, Wisconsin. She was awarded a National Science Foundation Academic Year Institute for the school year 1968 - 1969 at the University of Pennsylvania, Philadelphia, Pennsylvania. In May, 1969, she received a M. S. degree in education from the University of Pennsylvania. In September, 1969, she entered graduate school at the University of Florida as a teaching assistant in the Department of Chemistry. She received the DuPont Award for Excellence in teaching for the years 1969 - 1970 and 1970 - 1971. She served as an Interim Instructor during the 1970 - 1971 school year. In August, 1972 she was awarded the Tennessee Eastman-Kodak Fellowship for the current year.

Ms. Bergerud is married to Dr. Herbert F. Schaake. She is a member of the American Chemical Society.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

George E. Ryschkewitsch, Chairman
Professor of Chemistry

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R. Carl Stoufer.
Associate Professor of Chemistry

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Richard D. Dresdner
Professor of Chemistry

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Willis B. Person
Professor of Chemistry

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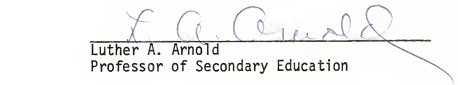

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This dissertation was submitted to the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1973

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